Published in Journal of Materials Chemistry 11, 2814 - 2831, 2001
which should be used for any reference to this work

Fullerene-containing liquid-crystalline dendrimers†

Blaise Dardel,[a] Daniel Guillon,*[b] Benoît Heinrich[b] and Robert Deschenaux*[a]

[a]*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case postale 2, CH-2007 Neuchâtel, Switzerland. Fax: +41 32 718 25 11; E-mail: robert.deschenaux@unine.ch*
[b]*Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 23 Rue du Loess, 67037 Strasbourg Cédex, France*

Addition reaction of mesomorphic malonate-based dendrimers (up to the fourth generation) with C_{60} gave liquid-crystalline fullerene derivatives. The cyanobiphenyl unit was used as liquid-crystalline promoter. The malonates presented nematic and/or smectic A phases. The fullerenes showed only smectic A phases, with the exception of the second generation dendrimer for which smectic A and nematic phases were observed. The supramolecular organization of the fullerene-based molecular units within the smectic A layers was investigated by X-ray diffraction. Two structural regimes were determined. For the low generation dendrimers, the supramolecular organization is determined by steric factors. For the high generation dendrimers, the mesogenic groups impose a microphase organization: due to lateral extension of the branching part of the molecule, the cyanobiphenyl groups arrange in a parallel fashion as in classical smectic A phases, the rest of the macromolecule being located between the mesogenic sublayers.

Introduction

The covalent functionalization of the [60]fullerene (C_{60}) with dendritic addends was first reported by Fréchet *et al.* and proved to be an elegant and effective method for the design of C_{60} derivatives with polymer properties.[1] After this pioneering work, other fullerene-based dendrimers were prepared and led to enthusiastic studies in supramolecular chemistry, materials science and medicinal chemistry: 1) a dendritic addend containing carboxylic acid functions was used to solubilize C_{60} in water,[2] 2) the modification of C_{60} with hydrophilic dendrons led to amphiphilic fullerenes which gave rise to stable Langmuir and Langmuir–Blodgett films,[3,4] and membranes,[5] 3) chiral[6] or non-chiral[7] dendritic hexa-adducts of fullerenes were obtained by functionalizing C_{60} with two different addends, and 4) globular dendrimers containing the porphyrin chromophore were designed to mimic natural metalloproteins.[8] In the above-mentioned examples, C_{60} is located at the center of the molecule. Nierengarten[9] reported fullerene-based dendrimers in which C_{60} is situated either at the periphery[10] or at the branching points[11] of the dendrimers. This approach is interesting for the elaboration of fullerene-rich materials.[12] Finally, non-covalent supramolecular complexes, obtained from C_{60} and various polybenzyl ether dendrimers, were reported.[13]

We are interested in fullerene-containing thermotropic liquid crystals. Two objectives motivate this research: 1) the understanding of how a sphere-like structure can be incorporated into liquid-crystalline phases (this study will lead to a better understanding of the structure–organization relationship for fullerene-based supramolecular assemblies), and 2) the design of new anisotropic materials.

The first concept we developed for the elaboration of liquid-crystalline fullerenes, addition of mesomorphic malonates to C_{60} by adapting the Bingel reaction,[14] led to a variety of liquid-crystalline mono- and hexa-adduct derivatives.[15–18] The cholesterol (for the mono-adduct derivatives[15–17]) and cyanobiphenyl (for the hexa-adduct derivative[18]) units were used as liquid-crystalline promoters. The fullerenes displayed smectic A phases. Recently, we reported the first liquid-crystalline fulleropyrrolidine.[19] The latter was prepared by 1,3-dipolar cycloaddition from a mesomorphic aldehyde derivative and sarcosine to C_{60} by following well-established literature procedures.[20] The fullerene derivative displayed a smectic A phase. Undoubtedly, the functionalization of C_{60} with liquid-crystalline addends is a suitable method for the elaboration of fullerene-containing thermotropic liquid crystals.

Owing to its size and shape, C_{60} decreases the liquid-crystalline tendency of the addend: C_{60} acts as a bulky spacer between the molecular units. This behavior could be circumvented either by carrying out a hexa-addition[18] or by using a second generation dendritic addend.[17,19,21] In both cases, the large number of mesogenic groups compensated the influence of C_{60}.

The use of dendritic addends could be an interesting means for the elaboration of fullerene-containing liquid crystals with tailor-made properties. The properties could be controlled *via* the dendrimer generation. Obviously, the influence of C_{60} on the thermal and mesomorphic behavior for a series of homologous dendritic materials has to be understood for the elaboration of materials displaying desired properties.

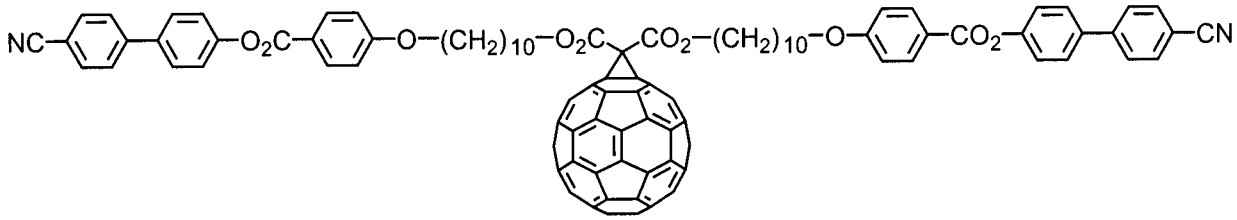
We report, herein, the synthesis, characterization, liquid-crystalline properties and supramolecular organization of a homologous family of fullerene-containing thermotropic liquid-crystals obtained from mesomorphic dendritic malonates (up to the fourth generation). The dendrimers were prepared by applying a convergent synthetic methodology.[22] Non-dendritic materials were also synthesized and used as model compounds. The cyanobiphenyl framework was used as liquid-crystalline promoter.

Results and discussion

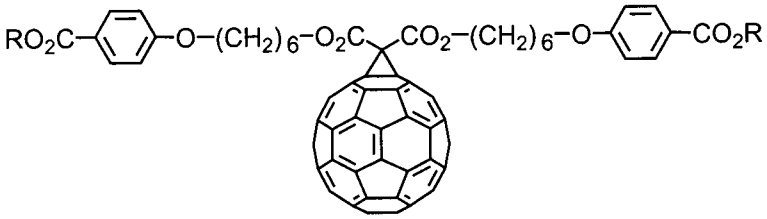
Design

This study is based on three types of structures: i) the model compounds **1** and **2** (Fig. 1), ii) the dendritic structures **3**–**6**

†Basis of a presentation given at Materials Discussion No. 4, 11–14 September 2001, Grasmere, UK.



1



2

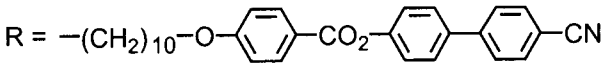


Fig. 1 Structures of model compounds **1** and **2**.

(Fig. 2) and iii) the hemi-dendritic structures **7** and **8** (Fig. 3). These compounds were designed to emphasize i) the influence of the number of alkyl chains included in the mesomorphic promoter (two chains in **1** and four chains in **2**), and ii) the influence of the dendrimer generation (**3** and **7**: first generation, **4** and **8**: second generation, **5**: third generation, **6**: fourth generation) on the thermal and liquid-crystalline properties. Note that the generation number 0 is assigned to the model compound **2**.

Syntheses

The preparation of **1**–**8** required the synthesis of the corresponding malonate followed by the addition of the malonate to C_{60} in the presence of I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Scheme 1 shows the synthesis of the liquid-crystalline promoter **9**. Treatment of 10-bromodecanol (**10**) with 4-hydroxybenzoic acid (**11**) gave intermediate **12**, the carboxylic acid function of which was esterified with 4-hydroxycyanobiphenyl (**13**) to give **9**.

The synthesis of **1** is presented in Scheme 2. Condensation of **9** with malonyl chloride (**14**) gave malonate derivative **15**. Addition of the latter to C_{60} furnished **1**.

The synthesis of **2** is illustrated in Scheme 3. Esterification of diacid **16**[17] with **9** gave malonate **17**, the addition of which to C_{60} led to **2**.

The synthesis of the first generation dendrimer **3** is depicted in Scheme 4. Esterification of diacid **18**[23] with **9** gave protected branch **19**. Removal of the silyl protecting group with $Zn(BF_4)_2$ gave phenol intermediate **20**, which was condensed with **16**[17] to give malonate **21**. Addition of **21** to C_{60} furnished **3**.

The synthesis of the second generation dendrimer **4** (Scheme 5), third generation dendrimer **5** (Scheme 6) and fourth generation dendrimer **6** (Scheme 7) is based on the convergent growth of the intermediate phenol derivative, which is prepared by reacting diacid **18**[23] with the phenol obtained from the preceding dendrimer generation, followed by the deprotection of the silyl substituent with $Zn(BF_4)_2$. Esterification of the phenol derivative with diacid **16**[17] gave the corresponding malonate, which was used in the addition reaction with C_{60}. In ref. 23, **18** was used in an elegant convergent synthesis of aryl ester dendrimers.

The deprotection of the silyl group depended on the quality of $Zn(BF_4)_2$ used. If the reaction does not proceed at room temperature as carried out here (see Experimental section), it can be conducted at 50–60 °C.[24]

The synthesis of hemi-dendrimers **7** (Scheme 8) and **8** (Scheme 9) required the preparation of **33** (Scheme 8) which was obtained by condensation of ethyl malonyl chloride (**31**) with **32**.[25] Esterification of the latter with either **20** or **23** gave malonate derivatives **34** and **35**, respectively, which were used in the addition reaction with C_{60}.

The structure and purity of all of the compounds were confirmed by ^{1}H NMR spectroscopy and elemental analysis. The ^{13}C NMR spectra were recorded only up to the first dendrimer generation; from the second generation dendrimer, ^{13}C NMR analysis would have required too large amounts of materials.

The fullerene and malonate derivatives showed similar ^{1}H NMR spectra (see Experimental section). The malonates gave an additional signal arising from the RO_2C–CH_2–CO_2R group. The UV–vis spectra of the fullerenes (see Experimental section) are in agreement with the [6,6]-closed methanofullerene structure.[26] The spectrum of dendrimer **6** is shown as a representative example in Fig. 4. The fullerenes retained the solubility properties of the malonates and were found to be soluble in common organic solvents.

Liquid-crystalline behavior

The liquid-crystalline and thermal properties of the mesomorphic promoter, malonate derivatives and fullerene derivatives were investigated by a combination of polarized optical miscroscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures and enthalpy changes are reported in Table 1. The mesomorphic behavior of the phenol and silyl intermediates was not examined. Their

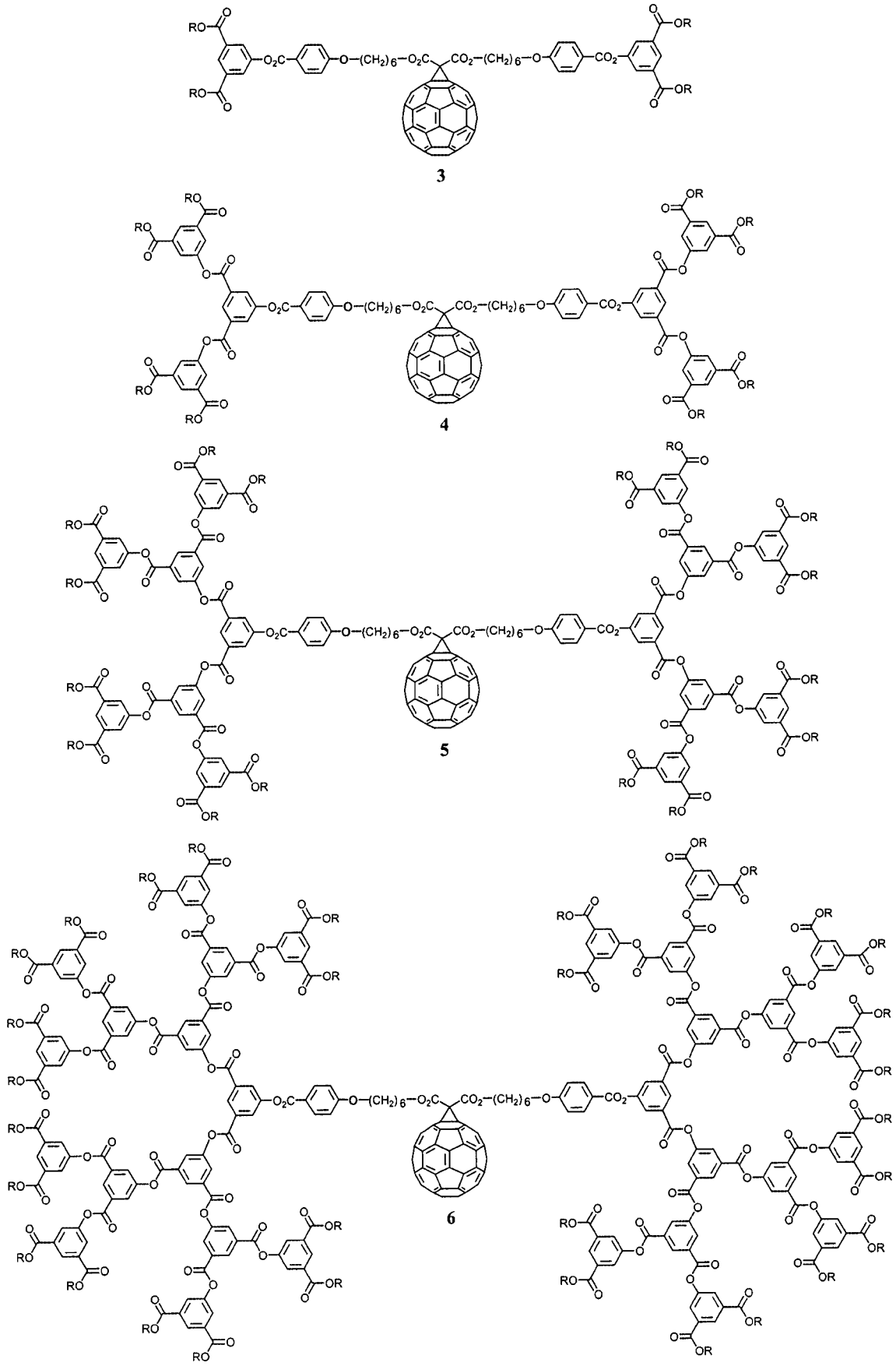


Fig. 2 Structures of dendrimers **3**–**6**. For R, see Fig. 1.

melting (T_m) and/or clearing (T_c) points are reported in the Experimental section.

The cyanobiphenyl derivative **9** gave a nematic phase.

The malonates gave rise to nematic (**21**), smectic A (**27**, **30** and **35**) or smectic A and nematic (**15**, **17**, **24** and **34**) phases. Model compound **15** gave a higher clearing point than model compound **17**. This is the consequence of the additional chains in **17** which add flexibility. For the dendritic compounds, the

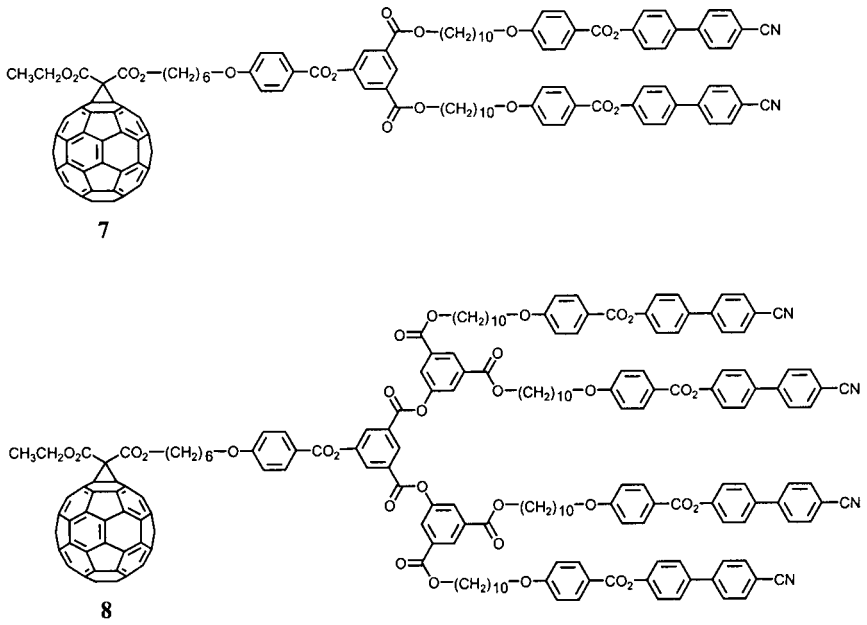
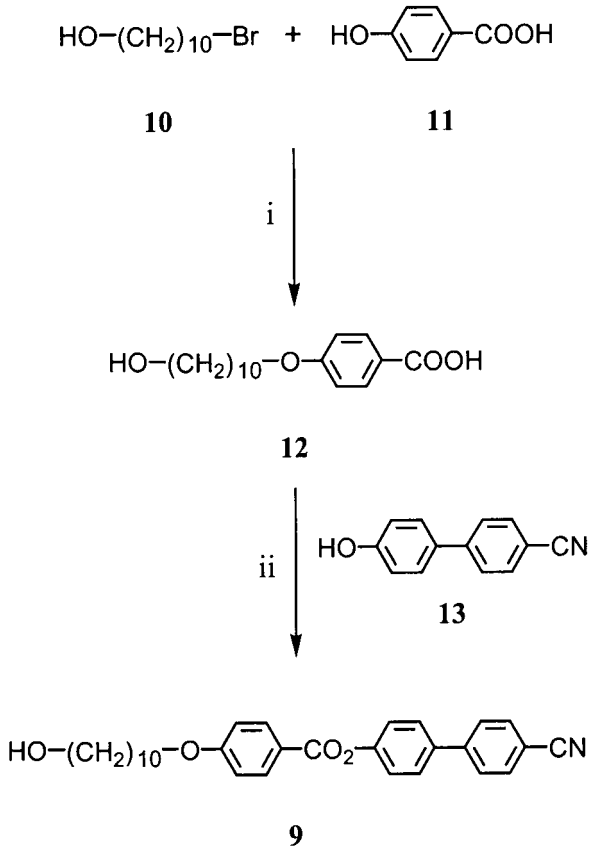


Fig. 3 Structures of hemi-dendrimers **7** and **8**.

stability of the liquid-crystalline state increased with the dendrimer generation: the higher the number of mesomorphic units, the higher the isotropization temperature. The hemi-dendrimers **34** and **35** also followed this trend.

Two features encountered for the malonates were found for the fullerene derivatives: compound **1**, with two flexible chains, showed a higher clearing point than **2** having four flexible chains, and the clearing point increased with the dendrimer generation.



Scheme 1 *Reagents and conditions:* i, aqueous NaOH, EtOH, reflux, 66%; ii, 4-(dimethylamino)pyridine (DMAP), *N,N′*-dicyclohexylcarbodiimide (DCC), CH_2Cl_2, room temperature, 81%.

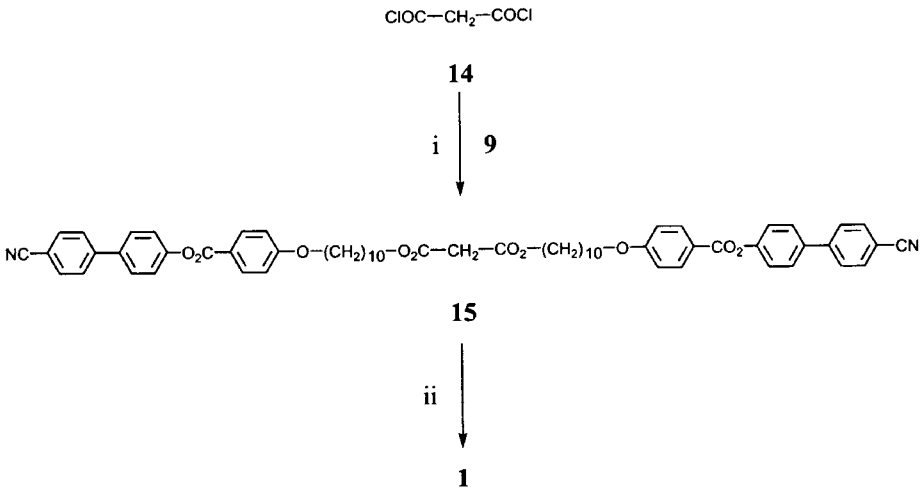
A striking difference between the fullerenes and the malonates of low generation resides in the liquid-crystalline phases which were observed: the fullerene derivatives exhibited only smectic A phases, with the exception of the second generation dendrimer **4**, which showed nematic and smectic A phases. This result is an indication that the sphere-like C_{60} unit governs, at least in part, the supramolecular organization of the mesomorphic units within the liquid-crystalline state. This behavior is clearly emphasized by comparing the mesomorphic behavior of malonate **21** (nematic phase) with that of its fullerene analogue **3** (smectic A phase). Finally, the fullerene derivatives gave clearing points which were lower than those of their malonate analogues.

The liquid-crystalline phases were identified by POM on the basis of their optical textures (nematic phase: homeotropic and schlieren textures; smectic A phase: homeotropic and focal conic textures). The narrow nematic phase displayed by **4** was clearly detected by DSC (Fig. 5). From the second dendrimer generation, glass transitions were recorded by DSC. This is in agreement with the non-crystalline character of the materials.

Supramolecular organization

To describe the molecular organization within the smectic A layers, it is necessary to take into account, at least for the low generation dendrimers and for an efficient space filling, the fact that the fullerene moiety has a cross-sectional area of about 90–100 $Å^2$,[27] whereas the mesogenic group has a cross-sectional area of about 22–25 $Å^2$.[28] In addition to these steric constraints, the molecular organization may be driven by specific interactions, such as: i) strong attractions between the fullerene moieties which could result in aggregation of the C_{60} units, ii) dipolar interactions through the strong terminal dipole moments of the mesogenic groups or iii) the natural tendency of the mesogenic groups to form an anisotropic organization within micro-domains. Finally, the amphipathic nature of these macromolecules can also be considered, resulting in micro-segregation of the polarizable and non-polarizable parts.

The X-ray diffraction patterns registered for all of the compounds are characteristic of smectic A phases. They contain, in the low angle region, two sharp reflections, the corresponding spacing of which is in the 1 : 2 ratio, and, in the wide angle region, a diffuse signal corresponding to the liquid-like arrangement of the mesogenic groups. For comparison purposes, all the *d*-layer spacings (in the smectic A phase) were



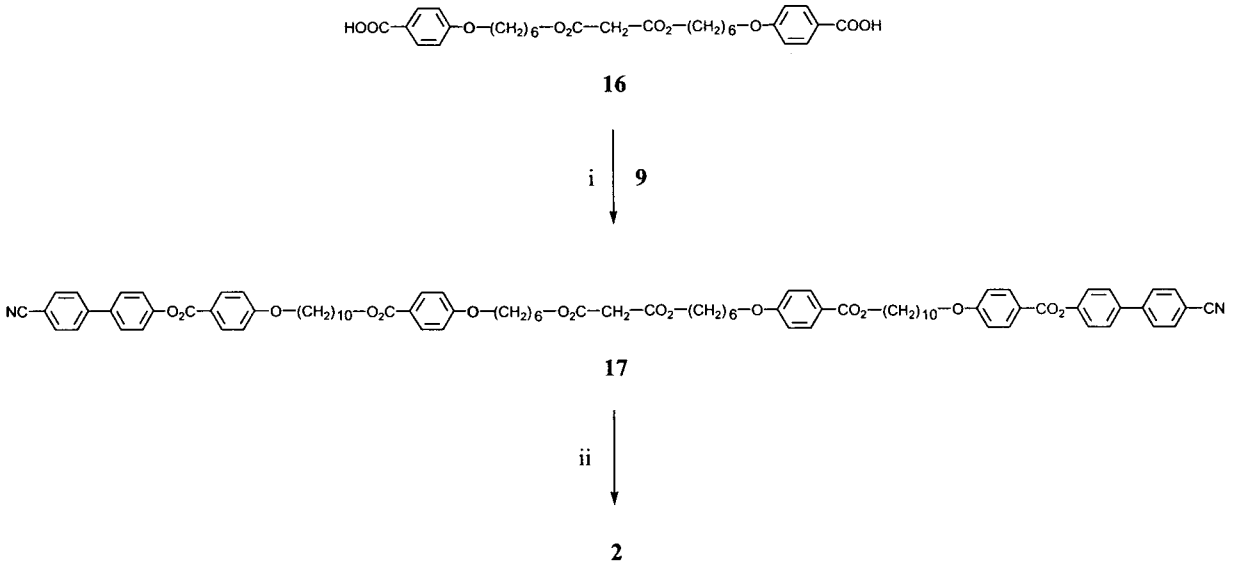
Scheme 2 *Reagents and conditions:* i, Et_3N, CH_2Cl_2, room temp., 92%; ii, C_{60}, I_2, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, room temperature, 22%.

determined at 140 °C. The variation of the layer thickness as a function of the generation number is represented in Fig. 6. Starting from values around 80 Å for the low generation dendrimers, the layer spacing decreases, and reaches a value of about 55 Å for the high generation dendrimers. Two regimes can be distinguished: the first one corresponds to spacings around 75–80 Å (for the low generation dendrimers), and the second one corresponds to spacings around 55–60 Å (for the high generation dendrimers). To understand this behavior, let us consider the supramolecular organization of each of the compounds within the smectic A phase.

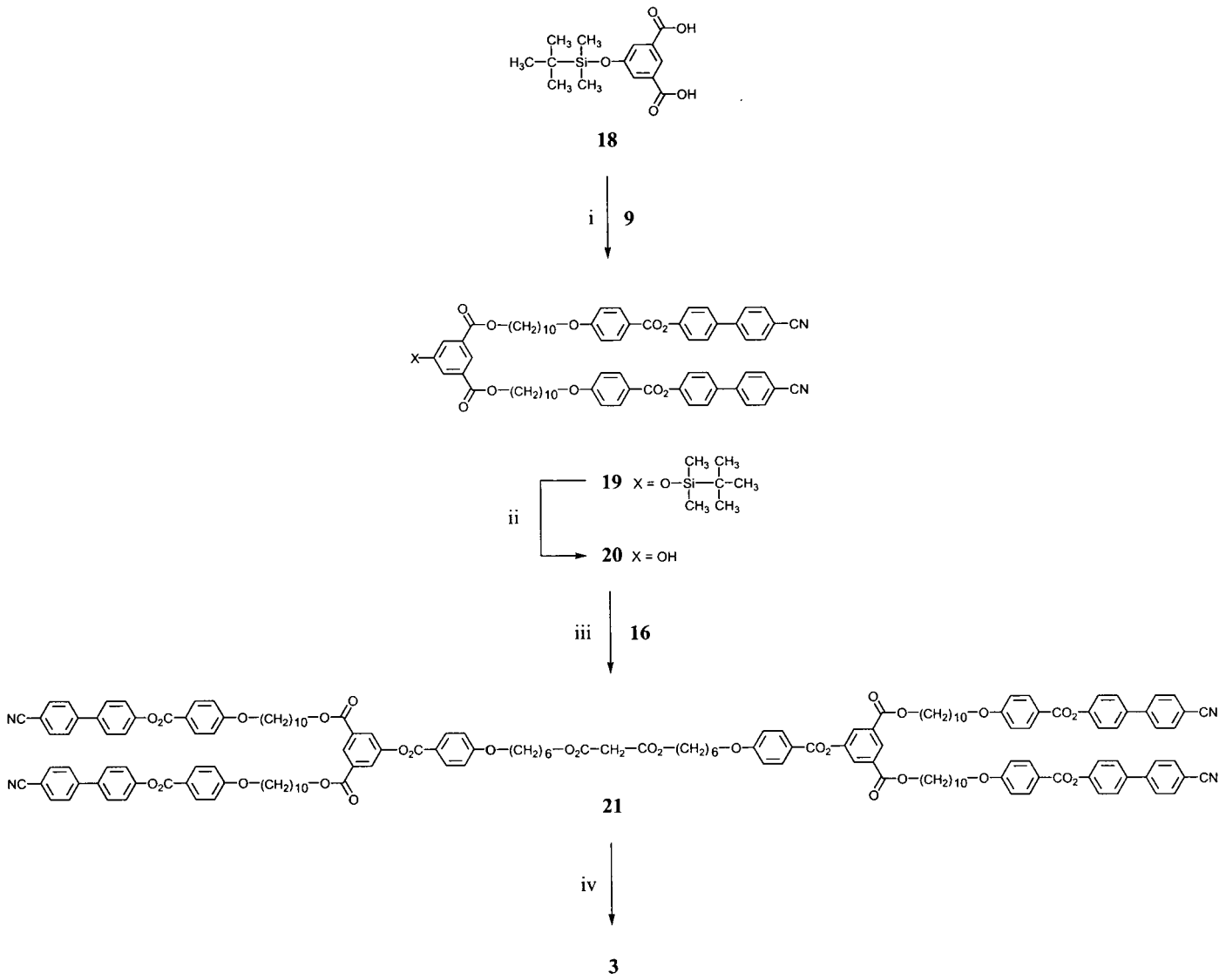
Compound 2 (zeroth generation dendrimer, $n=0$). The X-ray pattern of compound **2** is shown in Fig. 7. In addition to the reflections described above, it is interesting to note the presence of a diffuse band corresponding to a spacing of 8.5–9 Å. The layer spacing determined is 76 Å. The molecular organization within the smectic A layers is essentially governed by steric considerations, *i.e.* the necessary adequacy between the cross-sections of C_{60} and that of several mesogenic groups. Thus, the model proposed is based on the fact that the two arms of the molecule are folded towards the same direction and then the structure consists of a head-to-tail arrangement of such conformers. The value of the layer spacing observed is in agreement with the molecular dimensions (Fig. 8). The interdigitation is not complete, due to the volume occupied by the folded spacers close to the fullerene moiety. The diffuse band around 9 Å is attributed to lateral interactions between pairs of mesogenic groups.

As for **1**, in which the length of the arm attached to the malonate group is shorter by 15 Å when compared to **2**, the measured layer spacing is 57 Å. This value indicates that **1** organizes as **2**. Therefore, the supramolecular organizations of **1** and **2** within the smectic A layers are similar, and are mainly driven by steric considerations.

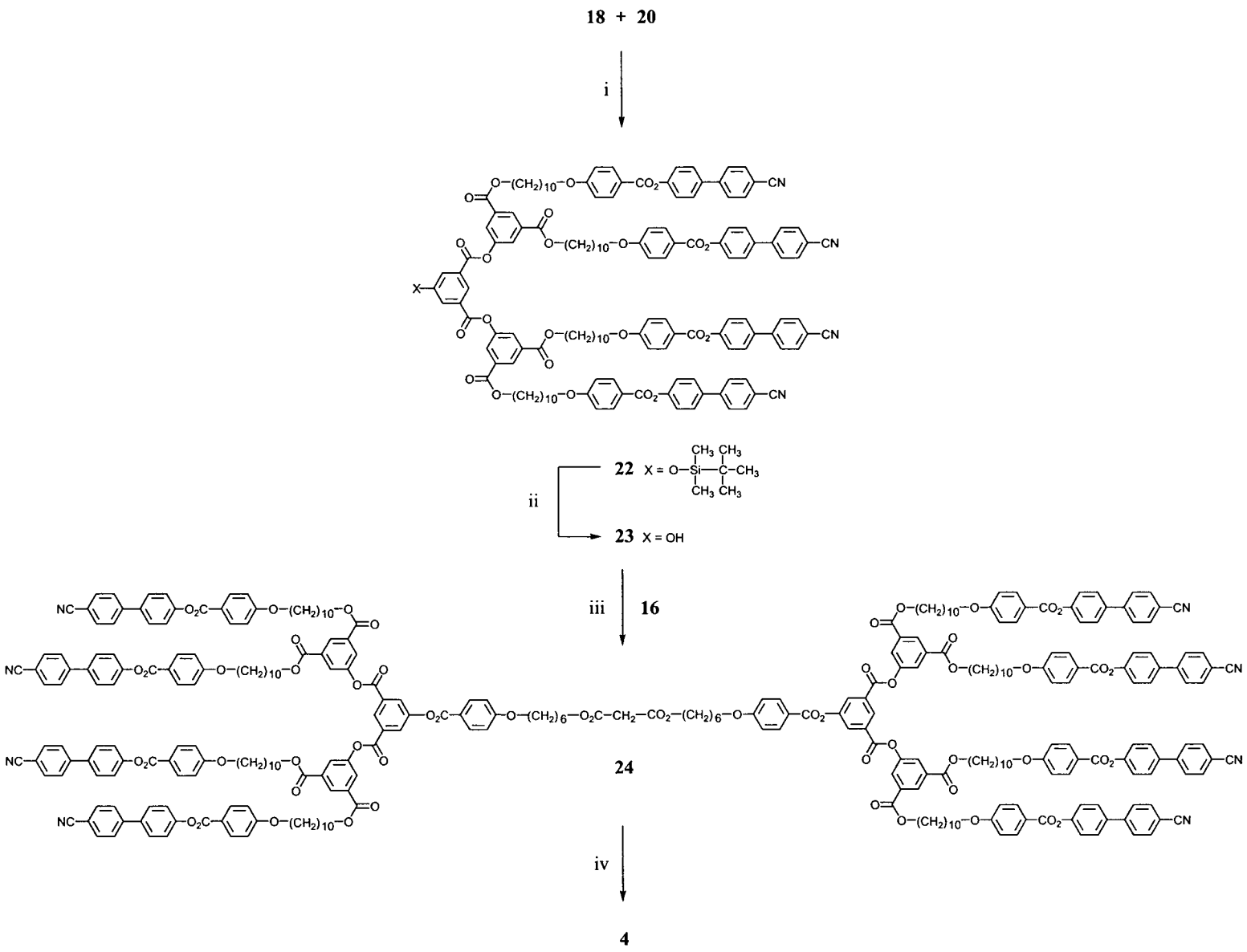
Compound 3 (first generation dendrimer, $n=1$). The layer spacing is 82 Å. This rather high value is, however, smaller than that expected for a pure double layer (105 Å) formed through dipolar interactions of the cyano groups attached at the end of the mesogenic parts (like, for example, in the S_{A2} phase of low molecular weight cyano compounds[29]). If we consider that the two spacers attached directly onto the malonate group tend to be parallel, a tentative explanation can be found in the molecular simulation of the molecule (Fig. 9): the molecule adopts a V-shape (the arms of the V being constituted by pairs



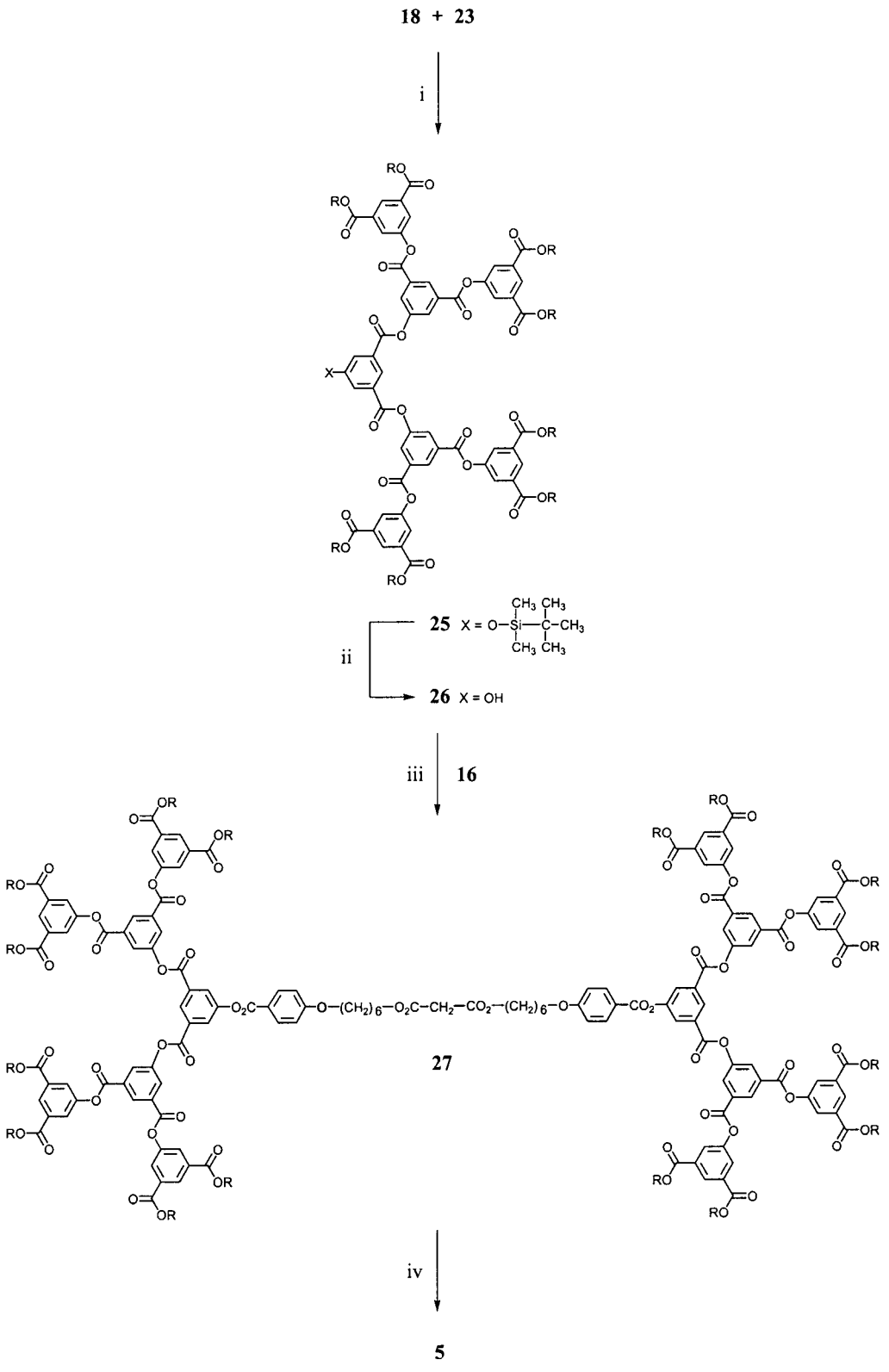
Scheme 3 *Reagents and conditions:* i, 4-(dimethylamino)pyridinium toluene-*p*-sulfonate (DPTS), DCC, 4-pyrrolidinopyridine (4-PPy), CH_2Cl_2, 0 °C and then room temperature, 51%; ii, C_{60}, I_2, DBU, toluene, room temperature, 50%.



Scheme 4 *Reagents and conditions:* i, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 95%; ii, $Zn(BF_4)_2$, H_2O, THF, room temperature, 91%; iii, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 53%; iv, C_{60}, I_2, DBU, toluene, room temperature, 29%.



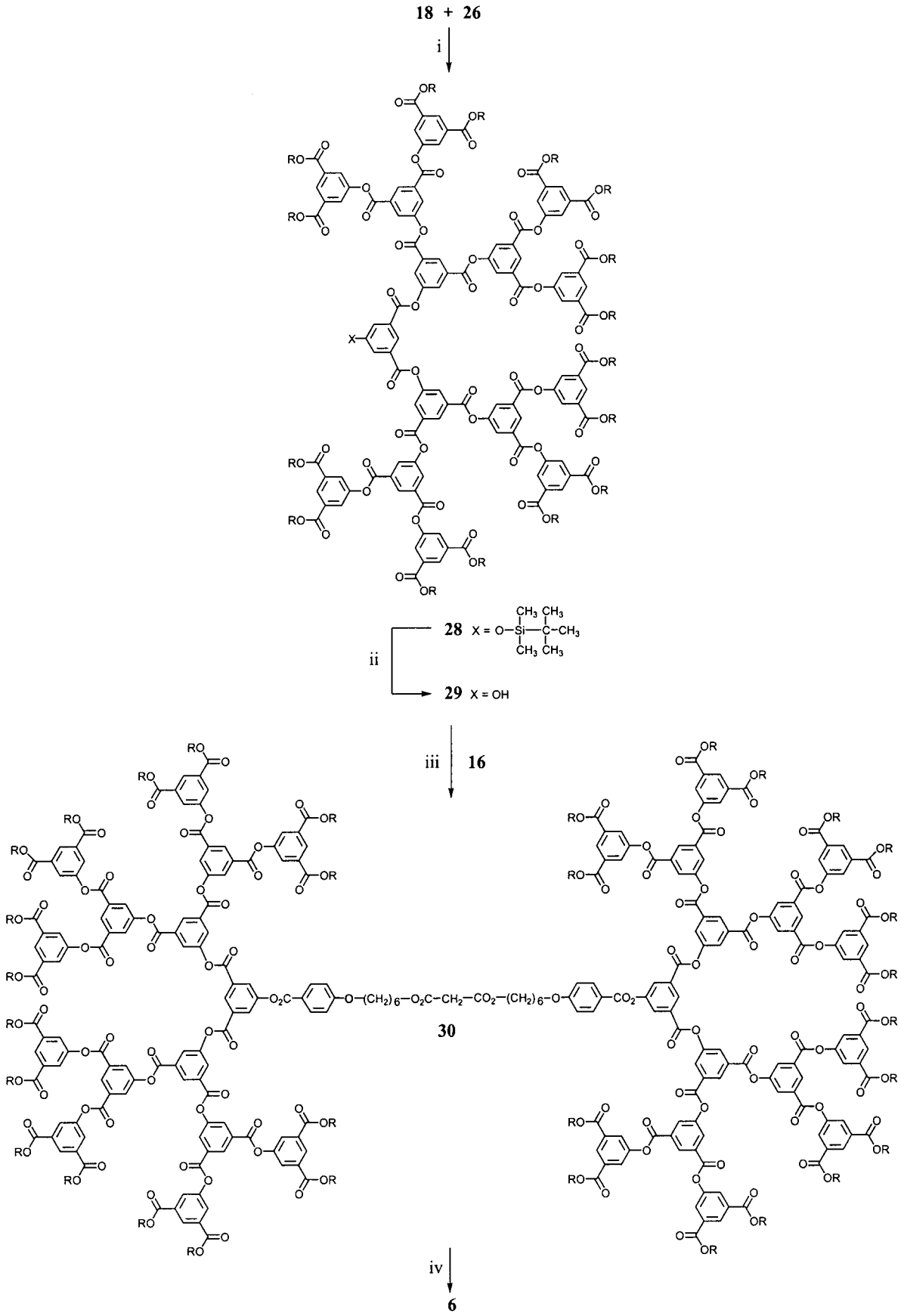
Scheme 5 *Reagents and conditions:* i, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 95%; ii, $Zn(BF_4)_2$, H_2O, THF, room temperature, 90%; iii, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 63%; iv, C_{60}, I_2, DBU, toluene, room temperature, 43%.



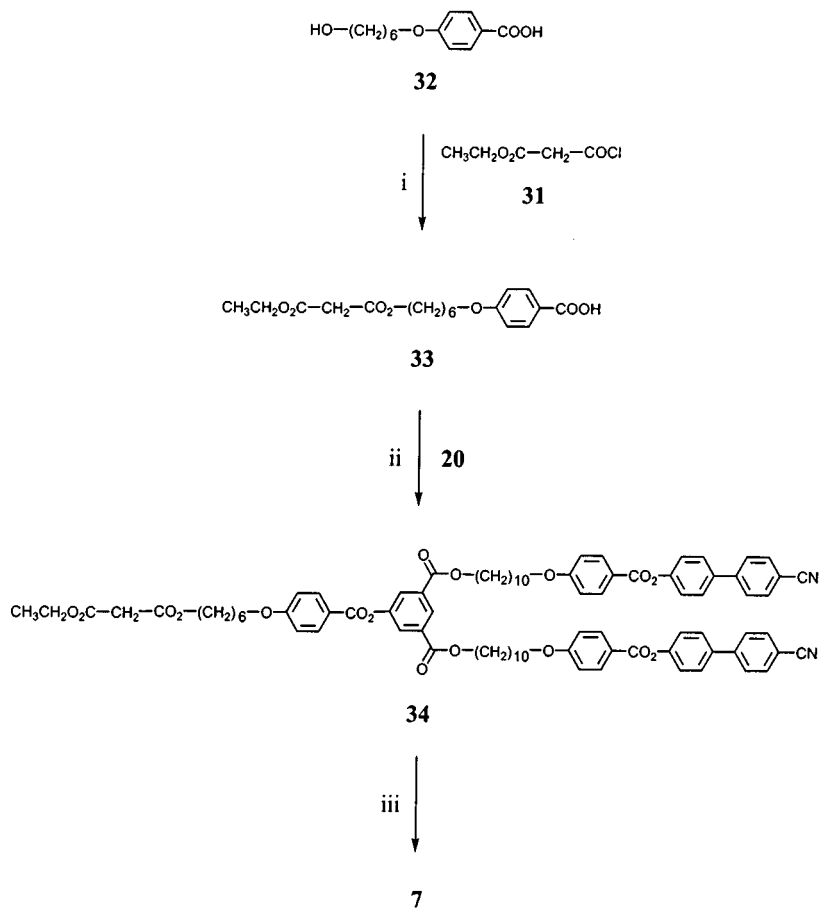
Scheme 6 *Reagents and conditions:* i, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 100%; ii, $Zn(BF_4)_2$, H_2O, THF, room temperature, 95%; iii, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 65%; iv, C_{60}, I_2, DBU, toluene, room temperature, 24%. For R, see Fig. 1.

of mesogenic groups), leaving enough space for mesogenic groups from adjacent layers to be included. Thus, a rather good space filling, due to the reasonable fit between the cross-sectional areas of fullerene and mesogenic groups, is achieved (Fig. 10).

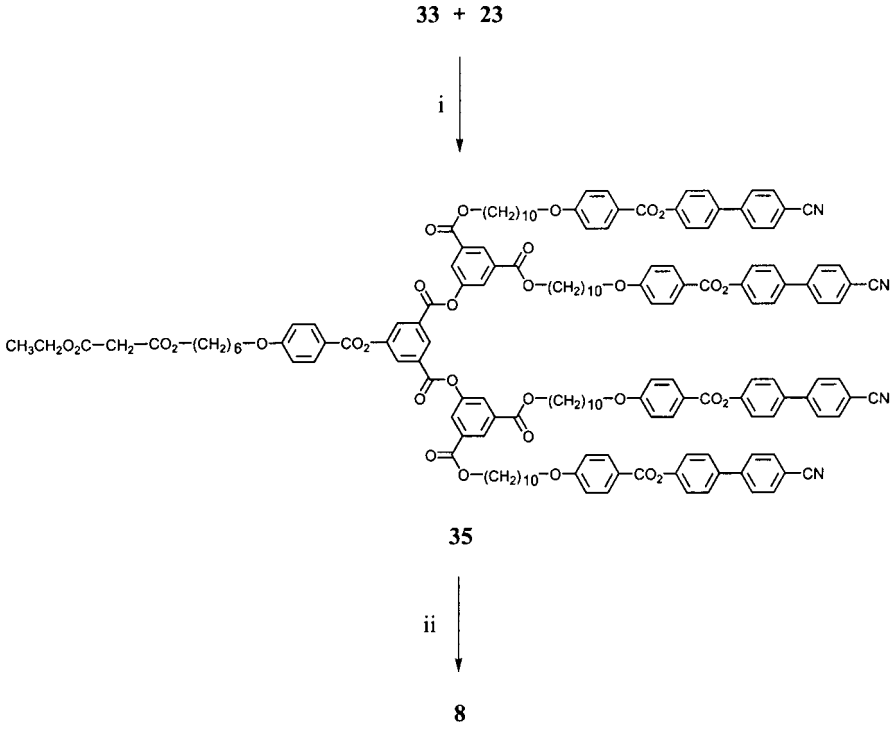
Compound 4 (second generation dendrimer, $n=2$). The measured layer spacing is 65 Å. This result is probably due to the branching part which begins to have significant lateral extension with respect to the normal to the layers, *i.e.* to the main orientation of the molecular axes of the mesogenic groups (Fig. 11). Such a lateral extension is due to the chemical structure itself, which allows free space between mesogenic groups on each side of the C_{60} moiety. Interpenetration from adjacent layers contributes to a good space filling and to the



Scheme 7 *Reagents and conditions:* i, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 65%; ii, $Zn(BF_4)_2$, H_2O, THF, room temperature, 85%; iii, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 70%; iv, C_{60}, I_2, DBU, toluene, room temperature, 21%. For R, see Fig. 1.



Scheme 8 *Reagents and conditions:* i, Et_3N, CH_2Cl_2, room temperature, 41%; ii, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 97%; iii, C_{60}, I_2, DBU, toluene, room temperature, 60%.



Scheme 9 *Reagents and conditions:* i, DPTS, DCC, 4-PPy, CH_2Cl_2, 0 °C and then room temperature, 100%; ii, C_{60}, I_2, DBU, toluene, room temperature, 54%.

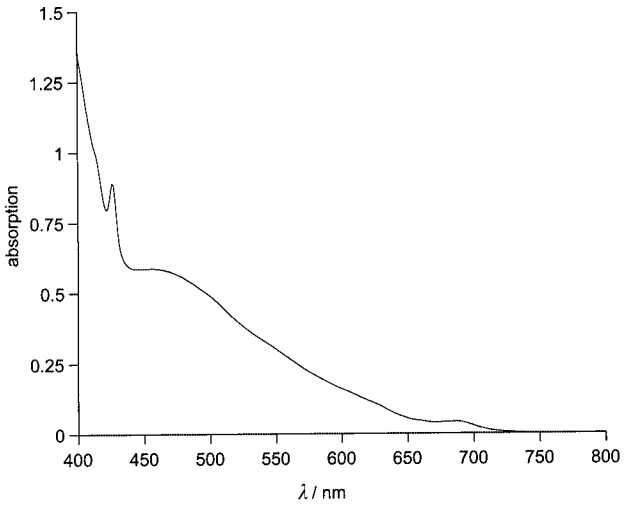


Fig. 4 Visible spectrum of dendrimer **6**.

Table 1 Phase transition temperatures of investigated compounds

Compound	T_g[a]/°C	Transition[b]	T/°C	ΔH/kJ mol^{-1}	ΔH/kJ mol^{-1} per mesogenic unit
9		Cr→N	122[c]	42	
		N→I	224[c]	0.9	0.9
15		Cr→S_A	129	95	
		S_A→N	225[d]		
		N→I	236	1.9	0.95
1	[e]	S_A→I	202	13	6.5
17		Cr→S_A	97[c]	83	
		S_A→N	153[c]		
		N→I	162[c]	5.5[f]	2.75
2	29	S_A→I	142	13	6.5
21	[e]	N→I	201[c]	5.4	1.4
3	48	S_A→I	179	18	4.5
24	46	S_A→N	196[c]		
		N→I	202[c]	21[f]	2.6
4	[e]	S_A→N	183		
		N→I	184	16[f]	2.0
27	[e]	S_A→I	232	56	3.5
5	[e]	S_A→I	212	57	3.6
30	[e]	S_A→I	259	198	6.2
6	[e]	S_A→I	252[c]	195	6.1
34	[e]	Cr→S_A	71[c]	51	
		S_A→N	138[d]		
		N→I	176[c]	2.8	1.4
7	[e]	S_A→I	155	11	5.5
35	34	S_A→ I	182	11	2.75
8	50	S_A→ I	161	12	3.0

[a]T_g = glass transition temperature. [b]S_A = smectic A phase, N = nematic phase, I = isotropic liquid. [c]First heating run. [d]Observed by polarized optical microscopy. [e]Not detected. [f]Overall enthalpy.

stabilization of the smectic A structure through an efficient lateral arrangement of the mesogenic groups. It is interesting to note the presence of a diffuse band in the X-ray pattern corresponding to a distance of 18 Å, which was assigned to the average lateral distance between fullerene moieties, in agreement with the organization proposed.

Compounds 5 (third generation dendrimer, $n=3$) and 6 (fourth generation dendrimer, $n=4$). For both compounds, the layer spacing in the smectic A phase is very similar and ranges between 56–57 Å. This value is rather small compared to the size of the dendrimers. In addition to the X-ray diffraction

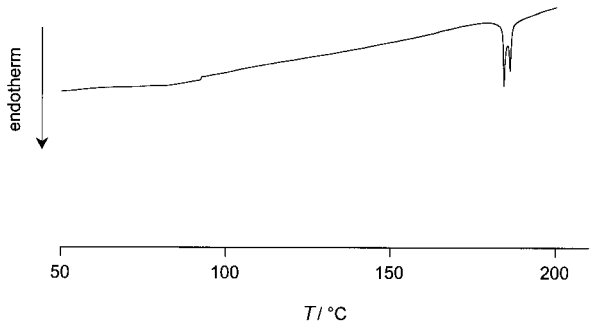


Fig. 5 Differential scanning calorimetry thermogram of **4** registered during the second heating run.

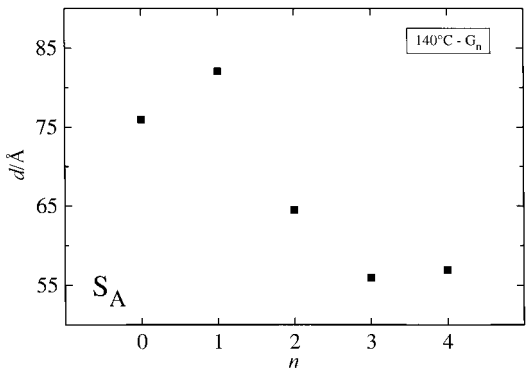


Fig. 6 Variation of the smectic A layer spacing as a function of the generation number; $n=0$: compound **2**, $n=1$: compound **3**, $n=2$: compound **4**; $n=3$: compound: **5**; $n=4$: compound **6**.

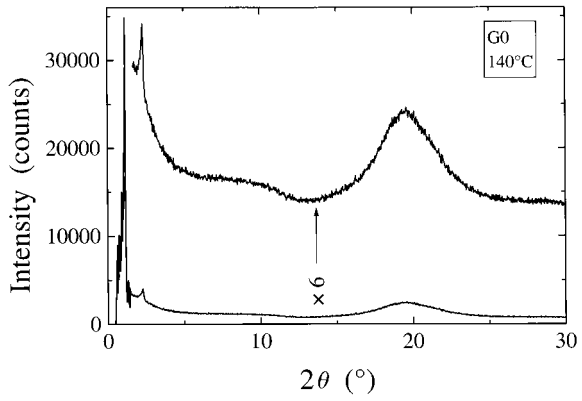


Fig. 7 X-Ray diffractogram pattern of **2** in the smectic A phase recorded at 140 °C.

signals characteristic of a smectic A phase, one should mention the presence of a diffuse band corresponding to a spacing of 22 and 29 Å for **5** and **6**, respectively. It is also important to remark that the intensity of the Bragg reflections decreases as the generation number increases, and that these reflections are not as sharp as for the low generation dendrimers.

To describe the molecular organization, it is necessary to realize that dendrimers **5** and **6** are mainly constituted of the branching nodes and of the 16 and 32 mesogenic moieties including the aliphatic spacers; the fullerene moiety represents a minor part. It is reasonable to admit that the structure is governed essentially by the polar cyano groups. The latter tend to form an anisotropic micro-domain and tend to be oriented parallel to one another. However, due to the fact that these groups are attached to one of their extremities and due also to the fact that the branching nodes are rather voluminous, their parallel orientation is far from being optimized. As is shown in

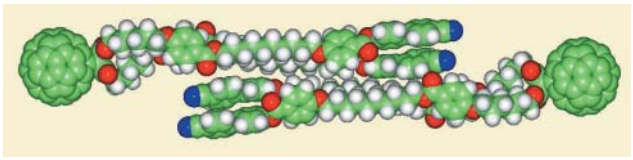


Fig. 8 Molecular simulation of the head-to-tail arrangement of **2** within the smectic A phase.

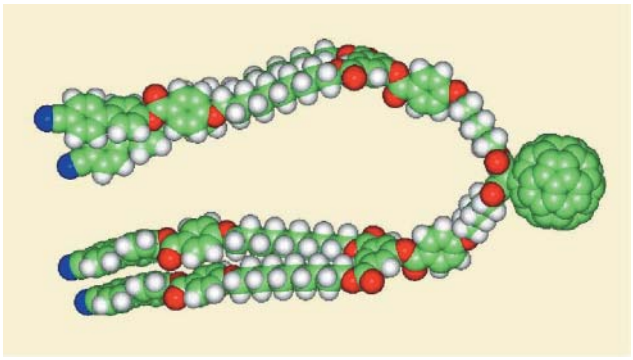


Fig. 9 Molecular simulation of **3** with the two arms pointing in the same direction and bearing a pair of cyanobiphenyl groups.

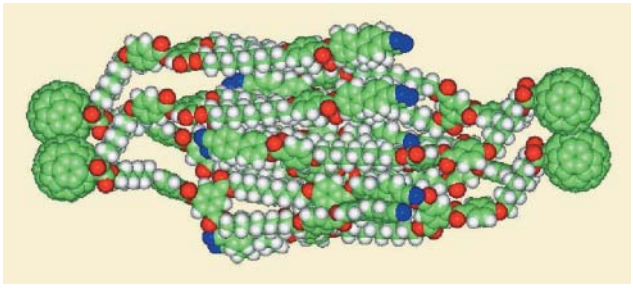


Fig. 10 Molecular simulation of the supramolecular organization of **3** within the smectic A layers.

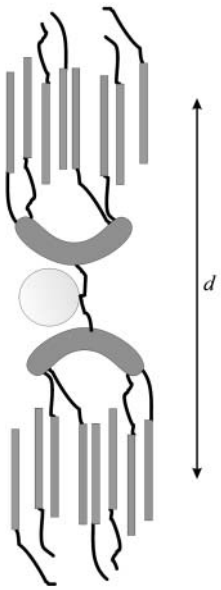


Fig. 11 Schematic representation of the supramolecular organization of **4** within the smectic A layers.

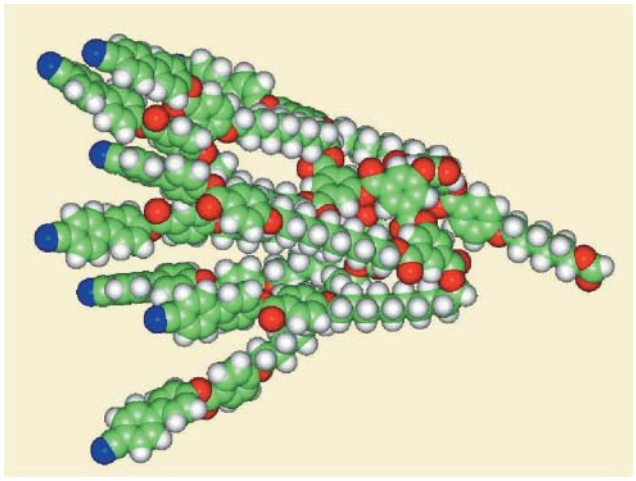


Fig. 12 Molecular simulation of half part of **5** showing the lateral extension of the branching part of the dendrimer and the cyanobiphenyl groups pointing to one main direction.

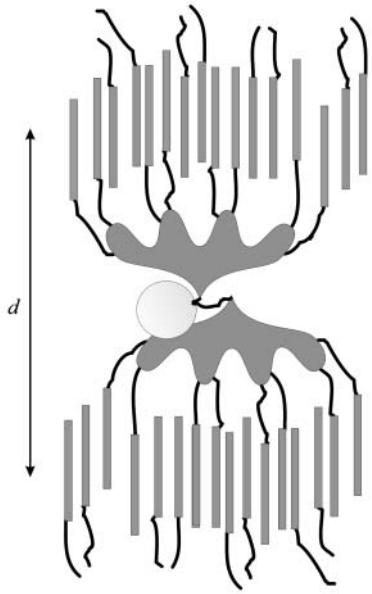


Fig. 13 Schematic representation of the supramolecular organization of **5** within the smectic A layers.

a molecular simulation for one half of the dendrimer **5** containing 8 mesogenic groups (Fig. 12), free space is available between the terminal cyano groups. Such a conformation favors interpenetration of mesogenic groups from adjacent layers. Thus, the molecular organization can be schematized as illustrated in Fig. 13 for dendrimer **5** (the molecular organization of **6** is the same; the only difference is the number of mesogenic groups). The central part of the layer is constituted by the fullerene moiety embedded by the important branching part (*i.e.* the dendrimer), and the layer interface is formed by the mesogenic cyano groups oriented in one main direction and partially interdigitated from one layer to the adjacent one. This interdigitation is in agreement with the decrease in intensity of the Bragg signals and with their simultaneous broadening; this is similar to X-ray investigations of the smectic A to nematic transition where the interface between the layers becomes more and more diffuse as the transition temperature is approached.[30] Let us remark that such an organization and the good space filling are presumably

made possible thanks to the presence of rather long aliphatic spacers and to a large number of ester groups which ensure the necessary flexibility of the dendrimer. Finally, in such a structure, the diffuse X-ray signals corresponding to spacings of 22 and 29 Å for **5** and **6**, respectively, may be attributed to the mean average distance between fullerene moieties within the smectic layers, this distance increasing as expected with the size of the dendrimer. This indicates that the expansion of the dendritic volume takes place essentially in two dimensions, as the dendrimer generation increases.

Malonates **27** and **30** exhibit also smectic A phases with a layer spacing value of 52 Å in both cases. This value is similar to that found for **5** and **6** and confirms that the fullerene moiety does not play a significant role in the supramolecular organization, which is governed by the large number of mesogenic groups.

Compounds 7 and 8. The layer spacings measured are 58 and 78 Å for **7** and **8**, respectively. Considering that the cross-sectional area of the fullerene moiety is about four times that of the mesogenic unit, the supramolecular organization of **7** within the smectic layers is straightforward and is similar to that represented in Fig. 8. It corresponds to the head-to-tail arrangement of individual molecules with a good agreement between the molecular dimensions and the observed layer spacing. It is interesting to compare **7** with **2**, which contains the same number of mesogenic groups but for which the layer spacing is much larger ($d = 76$ Å for **2**). The difference results in the fact that the two mesogenic groups are carried by one arm in **7**, whereas they are attached to two arms in **2**. This explains why the interdigitation is complete in **7** and incomplete in **2**, resulting in a significant difference in the layer spacing. As for **8**, for which the layer spacing is 78 Å, it is necessary to take into account the molecular design of this hemi-dendrimer. Similarly to **3**, which contains the same number of mesogenic groups, the molecular simulation suggests a V-shaped structure, in which space is available between pairs of mesogenic terminal groups, so that interdigitation between adjacent layers occurs. In such a description, the layer spacing of 78 Å fits the molecular dimensions of the model. Moreover, a good agreement exists between the cross-sections of four mesogenic groups and of the fullerene moiety. Thus, the molecular organization of **8** within the smectic A layers is identical to that described for **3**.

The malonates **15**, **17**, **21** and **24** display a nematic phase, in contrast to their fullerene derivatives (with the exception of **4** which also shows a nematic phase). This behavior indicates that i) the fullerene unit tends to prevent the occurence of nematic order, presumably because of its isotropic and large shape, and ii) the lateral extension of the branching part is so pronounced that no longitudinal sliding of the mesogenic groups in one main direction can take place.

Conclusion

The design and study of a family of fullerene-containing liquid-crystalline dendrimers allowed us to propose models for the organization of the fullerene-based molecular units within the liquid-crystalline phases.

For the low generation dendrimers (**1** and **2**), the organization is determined by steric factors: the supramolecular organization depends on the cross-sectional areas of the fullerene moiety and that of the mesogenic groups (to fill the space in an optimized way). For the high generation dendrimers (**3**, **4** and **5**), the mesogenic groups impose a microphase organization. Due to the lateral extension of the branching part, the cyano mesogenic groups are arranged in a parallel fashion as in classical smectic A phases. The almost constant value of the layer spacing found for the high generation dendrimers indicates that the branching part expands laterally with respect to the plane of the layers.

Comparison of the liquid-crystalline properties of the malonate derivatives with those of their fullerene counterparts strengthens the proposed models. On one hand, malonates **15** and **17** exhibit both smectic A and nematic phases, whereas their corresponding fullerene analogues **1** and **2** display only smectic A phases. This behavior confirms that for the low generation dendrimers containing the fullerene unit, the molecular organization is driven by steric constraints, producing only smectic A phases: a suitable adequacy between the cross-sectional areas of the fullerene moiety and that of the mesogenic groups has to be found. On the other hand, malonates **24**, **27** and **30** and their corresponding fullerene analogues **4**, **5** and **6** exhibit the same mesomorphic behavior, confirming the preponderant role of the cyano mesogenic groups.

A variety of fullerene derivatives with liquid-crystalline properties can be synthesized by applying the covalent (this work and references 15–19 and 21) or non-covalent[31] approach. The results obtained so far indicate that the design of fullerene-containing liquid crystals with tailor-made mesomorphic properties should be feasible.

Experimental

Materials

For the syntheses, CH_2Cl_2 (P_2O_5, under N_2) and toluene (NaH, under N_2) were distilled prior to use. Triethylamine (Fluka, puriss p.a.) and the other solvents were used as received. $Zn(BF_4)_2$ (hydrated with 6 to 7 molecules of water) was purchased from Aldrich; we used a molecular weight of 356.09. [60]Fullerene (99.5%) was purchased from Southern Chemical Group (Georgia, USA). Compounds **16**,[17] **18**,[23] and **32**[25] were prepared following literature procedures.

Techniques

Column chromatography used silica gel 60 (0.060–0.200 mm, SDS). Transition temperatures [onset point, second heating run (except indicated otherwise)] and enthalpies were determined with a differential scanning Mettler DSC 30 calorimeter connected to a Mettler TA 4000 processor, under N_2, at a rate of 10 °C min^{-1}; Mettler TA72.2/.5 Graphware was used for data treatment. For **4**, **24** and **34**, the transition temperatures and enthalpies were determined with a Mettler Toledo DSC 822^e calorimeter, under He, at a rate of 10 °C min^{-1}; Mettler STAR^e Software was used for data treatment. The melting (T_m) and clearing (T_c) points of the intermediates were determined during the first heating–cooling cycle; for the dendritic compounds, the glass transition temperatures (T_g) were not detected. Optical studies were made using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable temperature stage, under N_2. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer or a Bruker 400 spectrometer with the solvent as internal reference. UV–VIS spectra were recorded on a Kontron Uvikon Spectrophotometer 930. Modelling studies were performed using Biosym software running on a Silicon Graphics Indigo 2 system. For X-ray diffraction analyses, see ref. 32 Elemental analyses were done by Mikroelementar-analytisches Laboratorium ETH-Zurich.

Abbreviations

Column chromatography = CC; 4-(dimethylamino)pyridine = DMAP; *N*,*N*′-dicyclohexylcarbodiimide = DCC; 1,8-diazabicyclo[5.4.0]undec-7-ene = DBU; 4-(dimethylamino)pyridinium toluene-*p*-sulfonate = DPTS; 4-pyrrolidinopyridine = 4-PPy.

Syntheses

Compound 12. To a mixture of 4-hydroxybenzoic acid (**11**) (11.51 g, 83.33 mmol), EtOH (200 ml) and a 4 M NaOH aqueous solution (42 ml) heated under reflux, a solution of 10-bromodecanol (**10**) (15.10 g, 63.66 mmol) in EtOH (50 ml) was added dropwise. The mixture was stirred under reflux for 22 h, cooled to room temperature, acidified with a 3 M HCl aqueous solution (60 ml), and poured into ice. Purification of the precipitate by crystallization (isopropanol) gave pure **12** (12.35 g, 66%). $T_m = 119$ °C. ^{1}H NMR (200 MHz, $CDCl_3$ and a few drops of d_6-DMSO): δ 7.92 (d, 2 arom. H), 6.82 (d, 2 arom. H), 4.76 (br, 1 H, OH), 3.93 (t, 2 H, CH_2O), 3.53 (t, 2 H, CH_2OH), 1.8–1.6 (m, 2 H, CH_2CH_2O), 1.6–1.2 (14 H, CH_2CH_2OH and 12 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$ and a few drops of d_6-DMSO): δ 168.37, 162.69, 131.67, 122.70, 113.82, 68.00, 62.61, 32.64, 29.35, 29.30, 29.16, 28.94, 25.80, 25.63.

Compound 9. A mixture of **12** (7.60 g 25.82 mmol), 4-hydroxycyanobiphenyl (**13**) (5.15 g, 26.38 mmol), DMAP (3.24 g, 26.52 mmol), DCC (8.8 g, 43 mmol) and CH_2Cl_2 (300 ml) was stirred at room temperature for 20 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 1) gave pure **9** (9.82 g, 81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16 (d, 2 arom. H), 7.75 (d, 2 arom. H), 7.69 (d, 2 arom. H), 7.64 (d, 2 arom. H), 7.33 (d, 2 arom. H), 6.99 (d, 2 arom. H), 4.06 (t, 2 H, CH_2O), 3.65 (t, 2 H, CH_2OH), 1.9–1.7 (m, 2 H, CH_2CH_2O), 1.6–1.2 (14 H, CH_2CH_2OH and 12 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.82, 163.68, 151.55, 144.86, 136.67, 132.63, 132.33, 128.32, 127.67, 122.55, 121.17, 118.87, 114.34, 110.96, 68.32, 62.96, 32.74, 29.49, 29.44, 29.38, 29.31, 29.06, 25.94, 25.72. Anal. Calcd for $C_{30}H_{33}NO_4$ (471.60): C, 76.41; H, 7.05; N, 2.97%. Found: C, 76.37, H, 7.14, N, 3.01%.

Note: the synthesis of **9** can also be carried out in the presence of DPTS and 4-PPy instead of DMAP (for example, see the preparation of **17**).

Compound 15. To a mixture of **9** (376 mg, 0.797 mmol), malonyl chloride (**14**) (56 mg, 0.397 mmol) and CH_2Cl_2 (25 ml), was added a solution of Et_3N (80 mg, 0.791 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **15** (368 mg, 92%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16 (d, 4 arom. H), 7.75 (d, 4 arom. H), 7.68 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.32 (d, 4 arom. H), 6.98 (d, 4 arom. H), 4.15 (t, 4 H, CO_2CH_2), 4.05 (t, 4 H, CH_2O), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.7 (m, 4 H, CH_2CH_2O), 1.7–1.2 (28 H, $CO_2CH_2CH_2$ and 24 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.68, 164.78, 163.64, 151.52, 144.80, 136.65, 132.60, 132.31, 128.29, 127.63, 122.51, 121.16, 118.83, 114.30, 110.93, 68.28, 65.59, 41.65, 29.40, 29.28, 29.13, 29.04, 28.40, 25.93, 25.73. Anal. Calcd for $C_{63}H_{66}N_2O_{10}$ (1011.22): C, 74.83; H, 6.58; N, 2.77%. Found: C, 74.95; H, 6.73; N, 2.75%.

Compound 1. To a solution of C_{60} (241 mg, 0.334 mmol) in toluene (250 ml) were added a suspension of **15** (240 mg, 0.237 mmol) in toluene (20 ml), a solution of iodine (60 mg, 0.236 mmol) in toluene (20 ml) and DBU (72 mg, 0.473 mmol). The mixture was stirred at room temperature for 15 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with toluene–AcOEt 10 : 0.25) and precipitation (dissolution in CH_2Cl_2 followed by addition of AcOEt) gave pure **1** (90 mg, 22%). VIS (λ_{max} in nm (ε in dm^3 mol^{-1} cm^{-1}), CH_2Cl_2): 426 (2680), 486 (1610), 688 (210). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 4 arom. H), 7.74 (d, 4 arom. H), 7.69 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.97 (d, 4 arom. H), 4.51 (t, 4 H, CO_2CH_2), 4.04 (t, 4 H, CH_2O), 1.9–1.8 (m, 8 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.5–1.3 (24 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): 164.81, 163.69, 163.66, 151.55, 145.34, 145.24, 145.15, 144.84, 144.66, 144.58, 143.84, 143.07, 143.01, 142.94, 142.16, 141.88, 140.93, 138.95, 136.69, 132.64, 132.35, 128.33, 127.68, 122.55, 121.22, 118.86, 114.34, 110.97, 71.64, 68.31, 67.41, 52.45, 29.52, 29.49, 29.37, 29.20, 29.10, 28.58, 25.99. Anal. Calcd for $C_{123}H_{64}N_2O_{10}$ (1729.87): C, 85.40; H, 3.73; N, 1.62%. Found: C, 85.49; H, 3.98; N, 1.64%.

Compound 17. To a solution of **16** (167 mg, 0.307 mmol) in CH_2Cl_2 (50 ml) cooled to 0 °C were added a solution of DPTS (180 mg, 0.611 mmol), DCC (171 mg, 0.829 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (20 ml), and then a solution of **9** (290 mg, 0.615 mmol) in CH_2Cl_2 (80 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **17** (229 mg, 51%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16, (d, 4 arom. H), 7.98 (d, 4 arom. H), 7.74 (d, 4 arom. H), 7.68 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.99 (d, 4 arom. H), 6.89 (d, 4 arom. H), 4.28 (t, 4 H, ben-CO_2CH_2), 4.16 (t, 4 H, mal-CO_2CH_2), 4.05 (t, 4 H, $(CH_2)_9CH_2O$), 3.99 (t, 4 H, $(CH_2)_5CH_2O$), 3.37 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.6 (m, 16 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 32 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.63, 166.43, 164.81, 163.66, 162.73, 151.55, 144.83, 136.66, 132.61, 132.32, 131.49, 128.30, 127.65, 122.73, 122.54, 121.16, 118.85, 114.33, 113.95, 110.94, 68.31, 67.87, 65.41, 64.74, 41.57, 29.40, 29.28, 29.22, 29.04, 28.95, 28.73, 28.34, 25.99, 25.93, 25.59, 25.53. Anal. Calcd for $C_{89}H_{98}N_2O_{16}$ (1451.76): C, 73.63; H, 6.80; N, 1.93%. Found: C, 73.74; H, 6.96; N, 1.91%.

Compound 2. To a solution of C_{60} (126 mg, 0.175 mmol) in toluene (125 ml) were added a suspension of **17** (180 mg, 0.124 mmol) in toluene (50 ml), a solution of iodine (32 mg, 0.126 mmol) in toluene (10 ml) and DBU (38 mg, 0.250 mmol). The mixture was stirred at room temperature for 24 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with toluene–AcOEt 10 : 0.25) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into acetone) gave pure **2** (134 mg, 50%). VIS (λ_{max} in nm (ε in dm^3 mol^{-1} cm^{-1}), CH_2Cl_2): 426 (2780), 489 (1620), 687 (210). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, 4 arom. H), 7.97 (d, 4 arom. H), 7.74 (d, 4 arom. H), 7.69 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.98 (d, 4 arom. H), 6.88 (d, 4 arom. H), 4.51 (t, 4 H, $C_{60}CCO_2CH_2$), 4.28 (t, 4 H, ben-CO_2CH_2), 4.05 (t, 4 H, $(CH_2)_9CH_2O$), 4.00 (t, 4 H, $(CH_2)_5CH_2O$), 1.9–1.7 (m, 16 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.5–1.3 (m, 32 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.40, 164.81, 163.66, 162.67, 151.55, 145.25, 145.15, 145.05, 144.84, 144.64, 144.57, 143.83, 143.05, 142.98, 142.93, 142.14, 141.82, 140.91, 138.89, 136.66, 132.63, 132.32, 131.52, 128.32, 127.67, 122.79, 122.54, 121.17, 118.86, 114.34, 113.96, 110.94, 71.57, 68.31, 67.81, 67.23, 64.76, 52.34, 29.43, 29.29, 29.23, 29.04, 28.75, 28.51, 25.99, 25.94, 25.65. Anal. Calcd for $C_{149}H_{96}N_2O_{16}$ (2170.40): C, 82.46; H, 4.46; N, 1.29. Found: C, 82.54; H, 4.61; N, 1.20%.

Compound 19. To a suspension of **18** (1.57 g, 5.30 mmol) in CH_2Cl_2 (50 ml) cooled to 0 °C, were added a solution of DPTS (0.55 g, 1.87 mmol), DCC (5.45 g, 26.4 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (40 ml), and then a solution of **9** (5.01 g, 10.6 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **19** (6.08 g, 95%). $T_m = 96$ °C, $T_c = 193$ °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (t, 1 arom. H), 8.16 (d, 4 arom. H), 7.74 (d, 4 arom. H), 7.69 (d, 4 arom.

H), 7.68 (d, 2 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.98 (d, 4 arom. H), 4.33 (t, 4 H, CO_2CH_2), 4.05 (t, 4 H, CH_2O), 1.8–1.7 (m, 8 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 24 aliph. H); 1.00 (s, 9 H, $(CH_3)_3CSi$), 0.24 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.69, 164.79, 163.64, 155.81, 151.53, 144.81, 136.65, 132.61, 132.31, 132.11, 128.31, 127.64, 125.15, 123.48, 122.53, 121.15, 118.85, 114.31, 110.94, 68.29, 65.42, 29.43, 29.31, 29.20, 29.06, 28.61, 25.94, 25.58, 18.18, −4.47. Anal. Calcd for $C_{74}H_{82}N_2O_{11}Si$ (1203.55): C, 73.85; H, 6.87; N, 2.33%. Found: C, 73.89; H, 6.90; N, 2.22%.

Compound 20. To a solution of **19** (5.85 g, 4.86 mmol) in THF (200 ml), were added $Zn(BF_4)_2$ (4.2 g, 11.8 mmol) and H_2O (10 ml). The mixture was stirred at room temperature for 18 h, and THF was evaporated. Addition of water (100 ml) led to the formation of a precipitate which was removed by filtration. Trituration of the solid residue with hot AcOEt gave pure **20** (4.80 g, 91%). $T_m = 149\,^\circ C$, $T_c = 243\,^\circ C$. ^1H NMR (200 MHz, $CDCl_3$): δ 8.26 (t, 1 arom. H), 8.16 (d, 4 arom. H), 7.75 (d, 4 arom. H), 7.69 (d, 2 arom. H), 7.68 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.32 (d, 4 arom. H), 6.98 (d, 4 arom. H), 5.51 (s, 1 H, OH), 4.33 (t, 4 H, CO_2CH_2), 4.05 (t, 4 H, CH_2O), 1.9–1.7 (m, 8 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 24 aliph. H). Anal. Calcd for $C_{68}H_{68}N_2O_{11}$ (1089.29): C, 74.98; H, 6.29; N, 2.57%. Found: C, 74.92; H, 6.27; N, 2.60%.

Compound 21. To a solution of **16** (185 mg, 0.340 mmol) in CH_2Cl_2 (50 ml) cooled to 0 °C, were added a solution of DPTS (200 mg, 0.679 mmol), DCC (154 mg, 0.746 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (20 ml), and then a solution of **20** (740 mg, 0.679 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.25) gave pure **21** (488 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (t, 2 arom. H), 8.15 (d, 12 arom. H), 8.06 (d, 4 arom. H), 7.73 (d, 8 arom. H), 7.68 (d, 8 arom. H), 7.63 (d, 8 arom. H), 7.32 (d, 8 arom. H), 6.98 (d, 12 arom. H), 4.35 (t, 8 H, isoph-CO_2CH_2), 4.17 (t, 4 H, mal-CO_2CH_2), 4.05 (t, 4 H, $(CH_2)_5CH_2O$), 4.04 (t, 8 H, $(CH_2)_9CH_2O$), 3.39 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.6 (m, 24 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 56 aliph. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.64, 165.03, 164.78, 164.47, 163.70, 163.64, 151.52, 151.01, 144.79, 136.62, 132.59, 132.39, 132.29, 128.28, 127.86, 127.63, 127.26, 122.51, 121.13, 120.79, 118.83, 114.35, 114.30, 110.92, 68.28, 68.06, 65.70, 65.38, 41.55, 29.40, 29.36, 29.26, 29.17, 29.02, 28.91, 28.59, 28.34, 25.90, 25.88, 25.59, 25.52. Anal. Calcd for $C_{165}H_{168}N_4O_{30}$ (2687.15): C, 73.75; H, 6.30; N, 2.08%. Found: C, 73.59; H, 6.28; N, 2.10%.

Compound 3. To a solution of C_{60} (147 mg, 0.204 mmol) in toluene (150 ml), were added a suspension of **21** (450 mg, 0.167 mmol) in toluene (50 ml), a solution of iodine (44 mg, 0.173 mmol) in toluene (15 ml) and DBU (51 mg, 0.335 mmol). The mixture was stirred at room temperature for 15 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with toluene–AcOEt 10 : 0.25) and precipitation (dissolution in toluene and precipitation by pouring the solution into acetone) gave pure **3** (164 mg, 29%). VIS (λ_{max} in nm (ε in $dm^3\,mol^{-1}\,cm^{-1}$), CH_2Cl_2): 426 (2780), 488 (1640), 687 (210). ^1H NMR (200 MHz, $CDCl_3$): δ 8.59 (t, 2 arom. H), 8.15 (d, 8 arom. H), 8.13 (d, 4 arom. H), 8.05 (d, 4 arom. H), 7.74 (d, 8 arom. H), 7.68 (d, 8 arom. H), 7.63 (d, 8 arom. H), 7.32 (d, 8 arom. H), 6.98 (d, 12 arom. H), 4.53 (t, 4 H, $C_{60}CCO_2CH_2$), 4.35 (t, 8 H, isoph-CO_2CH_2), 4.05 (t, 4 H, $(CH_2)_5CH_2O$), 4.04 (t, 8 H, $(CH_2)_9CH_2O$), 2.0–1.6 (m, 24 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 56 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.02, 164.76, 164.43, 163.64, 151.53, 151.00, 145.24, 145.21, 145.13, 145.02, 144.80, 144.61, 144.55, 144.52, 143.79, 143.05, 142.98, 142.90, 142.11, 141.79, 140.91, 138.88, 136.62, 132.60, 132.43, 132.29, 128.29, 127.88, 127.63, 127.27, 122.52, 121.14, 120.85, 118.83, 114.31, 110.93, 71.55, 68.29, 68.00, 67.21, 65.71, 52.36, 29.37, 29.28, 29.19, 29.02, 28.60, 25.90, 25.62. Anal. Calcd for $C_{225}H_{166}N_4O_{30}$ (3405.80): C, 79.35; H, 4.91; N, 1.65%. Found: C, 79.14; H, 5.06; N, 1.62%.

Compound 22. To a suspension of **18** (544 mg, 1.84 mmol) in CH_2Cl_2 (50 ml) cooled to 0 °C, were added a solution of DPTS (907 mg, 3.08 mmol), DCC (1.71 g, 8.29 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (20 ml), and then a solution of **20** (4.01 g, 3.68 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure **22** (4.25 g, 95%). $T_c = 214\,^\circ C$. ^1H NMR (200 MHz, $CDCl_3$): δ 8.63 (t, 1 arom. H), 8.61 (t, 2 arom. H), 8.12 (d, 8 arom. H), 8.09 (d, 4 arom. H), 7.91 (d, 2 arom. H), 7.71 (d, 8 arom. H), 7.65 (d, 8 arom. H), 7.61 (d, 8 arom. H), 7.30 (d, 8 arom. H), 6.95 (d, 8 arom. H), 4.35 (t, 8 H, CO_2CH_2), 4.02 (t, 8 H, CH_2O), 1.9–1.6 (m, 16 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 48 aliph. H), 1.02 (s, 9 H, $(CH_3)_3CSi$), 0.29 (s, 6 H, $(CH_3)_2Si$). Anal. Calcd for $C_{150}H_{152}N_4O_{25}Si$ (2438.95): C, 73.87; C, 6.28; N, 2.30%. Found: C, 73.86; H, 6.37; N, 2.33%.

Compound 23. To a solution of **22** (3.60 g, 1.48 mmol) in THF (200 ml), were added $Zn(BF_4)_2$ (3.0 g, 8.4 mmol) and H_2O (10 ml). The mixture was stirred at room temperature for 18 h. Evaporation of THF gave a precipitate which was removed by filtration. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.25 and then 10 : 0.5) gave pure **23** (3.10 g, 90%). $T_c = 230\,^\circ C$. ^1H NMR (200 MHz, $CDCl_3$): δ 8.63 (t, 2 arom. H), 8.58 (t, 1 arom. H), 8.15 (d, 8 arom. H), 8.09 (d, 4 arom. H), 7.94 (d, 2 arom. H), 7.74 (d, 8 arom. H), 7.68 (d, 8 arom. H), 7.63 (d, 8 arom. H), 7.32 (d, 8 arom. H), 6.97 (d, 8 arom. H), 6.40 (br, 1 H, OH), 4.36 (t, 8 H, CO_2CH_2), 4.04 (t, 8 H, CH_2O), 1.9–1.7 (m, 16 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 48 aliph. H). Anal. Calcd for $C_{144}H_{138}N_4O_{25}$ (2324.69): C, 74.40; H, 5.98; N, 2.41%. Found: C, 74.33; H, 6.05; N, 2.41%.

Compound 24. To a solution of **16** (118 mg, 0.217 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C, were added a solution of DPTS (127 mg, 0.431 mmol), DCC (424 mg, 2.05 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **23** (1.01 g, 0.434 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.3 then 10 : 0.5) gave pure **24** (0.71 g, 63%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.93 (t, 2 arom. H), 8.63 (t, 4 arom. H), 8.35 (d, 4 arom. H), 8.17 (d, 4 arom. H), 8.14 (d, 16 arom. H), 8.10 (d, 8 arom. H), 7.74 (d, 16 arom. H), 7.67 (d, 16 arom. H), 7.63 (d, 16 arom. H), 7.31 (d, 16 arom. H), 6.99 (d, 4 arom. H), 6.97 (d, 16 arom. H), 4.36 (t, 16 H, isoph-CO_2CH_2), 4.17 (t, 4 H, mal-CO_2CH_2), 4.03 (t, 20 H, CH_2O), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.6 (m, 40 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 104 aliph. H). Anal. Calcd for $C_{317}H_{308}N_8O_{58}$ (5157.94): C, 73.82; H, 6.02; N, 2.17%. Found: C, 73.64; H, 6.15; N, 2.28%.

Compound 4. To a solution of C_{60} (210 mg, 0.291 mmol) in toluene (250 ml), were added a solution of **24** (581 mg, 0.113 mmol) in toluene (5 ml), a solution of iodine (28 mg, 0.113 mmol) in toluene (5 ml) and DBU (34 mg, 0.223 mmol). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with toluene–CH_2Cl_2–AcOEt 10 : 5 : 0.5) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into

MeOH) gave pure **4** (287 mg, 43%). VIS (λ_{max} in nm (ε in $dm^3\ mol^{-1}\ cm^{-1}$), CH_2Cl_2): 426 (2910), 489 (1700), 687 (200). ^1H NMR (200 MHz, $CDCl_3$): 8.93 (t, 2 arom. H), 8.63 (t, 4 arom. H), 8.34 (t, 4 arom. H), 8.14 (d, 20 arom. H), 8.11 (d, 8 arom. H), 7.74 (d, 16 arom. H), 7.67 (d, 16 arom. H), 7.63 (d, 16 arom. H), 7.31 (d, 16 arom. H), 6.97 (d, 20 arom. H), 4.53 (t, 4 H, $C_{60}CCO_2CH_2$), 4.36 (t, 16 H, isoph-CO_2CH_2), 4.03 (t, 20 H, CH_2O), 1.9–1.7 (m, 40 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 104 aliph. H). Anal. Calcd for $C_{377}H_{306}N_8O_{58}$ (5876.58): C, 77.05; H, 5.25; N, 1.91%. Found: C, 77.02; H, 5.49; N, 1.93%.

Compound 25. To a suspension of **18** (164 mg, 0.553 mmol) in CH_2Cl_2 (10 ml) cooled to 0 °C, were added a solution of DPTS (200 mg, 0.679 mmol), DCC (450 mg, 2.18 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (10 ml), and then a solution of **23** (2.51 g, 1.08 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **25** (2.65 g, 100%). $T_c = 233$ °C. ^1H NMR (200 MHz, $CDCl_3$): δ 8.97 (t, 2 arom. H), 8.68 (t, 1 arom. H), 8.63 (t, 4 arom. H), 8.39 (d, 4 arom. H), 8.13 (d, 16 arom. H), 8.11 (d, 8 arom. H), 7.96 (d, 2 arom. H), 7.73 (d, 16 arom. H), 7.67 (d, 16 arom. H), 7.62 (d, 16 arom. H), 7.31 (d, 16 arom. H), 6.96 (d, 16 arom. H), 4.36 (t, 16 H, CO_2CH_2), 4.03 (t, 16 H, CH_2O), 1.9–1.7 (m, 32 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 96 aliph. H), 1.04 (s, 9 H, $(CH_3)_3CSi$), 0.31 (s, 6 H, $(CH_3)_2Si$). Anal. Calcd for $C_{302}H_{292}N_8O_{53}Si$ (4909.74): C, 73.88; H, 5.99; N, 2.28%. Found: C, 73.66; H, 6.19; N, 2.35%.

Compound 26. To a solution of **25** (2.65 g, 0.540 mmol) in THF (100 ml), were added $Zn(BF_4)_2$ (2.1 g, 5.9 mmol) and H_2O (5 ml). The mixture was stirred at room temperature for 18 h. Evaporation of THF gave a precipitate which was removed by filtration. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.25) gave pure **26** (2.46 g, 95%). $T_c = 247$ °C. ^1H NMR (200 MHz, $CDCl_3$): δ 8.97 (t, 2 arom. H), 8.63 (t, 4 arom. H), 8.59 (t, 1 arom. H), 8.36 (d, 4 arom. H), 8.14 (d, 16 arom. H), 8.11 (d, 8 arom. H), 7.95 (d, 2 arom. H), 7.73 (d, 16 arom. H), 7.66 (d, 16 arom. H), 7.62 (d, 16 arom. H), 7.31 (d, 16 arom. H), 6.96 (d, 16 arom. H), 4.36 (t, 16 H, CO_2CH_2), 4.02 (t, 16 H, CH_2O), 1.9–1.7 (m, 32 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 96 aliph. H). Anal. Calcd for $C_{296}H_{278}N_8O_{53}$ (4795.47): C, 74.14; H, 5.84; N, 2.34%. Found: C, 74.01; H, 5.95; N, 2.32%.

Compound 27. To a solution of **16** (57 mg, 0.105 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C, were added a solution of DPTS (57 mg, 0.194 mmol), DCC (88 mg, 0.427 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **26** (1.00 g, 0.209 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5 then 10 : 1) gave pure **27** (684 mg, 65%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.97 (t, 6 arom. H), 8.63 (t, 8 arom. H), 8.40 (d, 12 arom. H), 8.13 (d, 36 arom. H), 8.11 (d, 16 arom. H), 7.73 (d, 32 arom. H), 7.66 (d, 32 arom. H), 7.62 (d, 32 arom. H), 7.30 (d, 32 arom. H), 6.96 (d, 36 arom. H), 4.35 (t, 32 H, isoph-CO_2CH_2), 4.16 (t, 4 H, mal-CO_2CH_2), 4.02 (t, 36 H, CH_2O), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.7 (m, 72 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 200 aliph. H). Anal. Calcd. for $C_{621}H_{588}N_{16}O_{114}$ (10099.52): C, 73.85; H, 5.87; N, 2.22%. Found: C, 73.69; H, 5.94; N, 2.25%.

Compound 5. To a solution of C_{60} (65 mg, 0.090 mmol) in toluene (100 ml), were added a solution of **27** (451 mg, 0.045 mmol) in CH_2Cl_2 (5 ml), a solution of iodine (11 mg, 0.043 mmol) in toluene (5 ml) and DBU (14 mg, 0.092 mmol). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with CH_2Cl_2–AcOEt 10 : 0.5) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into acetone) gave pure **5** (115 mg, 24%). VIS (λ_{max} in nm (ε in $dm^3\ mol^{-1}\ cm^{-1}$), CH_2Cl_2): 426 (4390), 462 (2900), 688 (210). ^1H NMR (200 MHz, $CDCl_3$): δ 8.98 (t, 6 arom. H), 8.62 (t, 8 arom. H), 8.40 (d, 8 arom. H), 8.39 (d, 4 arom. H), 8.13 (d, 36 arom. H), 8.11 (d, 16 arom. H), 7.72 (d, 32 arom. H), 7.66 (d, 32 arom. H), 7.61 (d, 32 arom. H), 7.30 (d, 32 arom. H), 6.95 (d, 36 arom. H), 4.52 (t, 4 H, $C_{60}CCO_2CH_2$), 4.35 (t, 32 H, isoph-CO_2CH_2), 4.02 (t, 36 H, CH_2O), 1.9–1.6 (m, 72 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.3–1.6 (m, 200 aliph. H). Anal. Calcd for $C_{681}H_{586}N_{16}O_{114}$ (10818.16): C, 75.61; H, 5.46; N, 2.07%. Found: C, 75.69; H, 5.62; N, 2.08%.

Compound 28. To a suspension of **18** (62 mg, 0.209 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C were added a solution of DPTS (75 mg, 0.255 mmol), DCC (186 mg, 0.901 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **26** (2.02 g, 0.421 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 1) gave pure **28** (1.34 g, 65%). $T_c = 254$ °C. ^1H NMR (200 MHz, $CDCl_3$): δ 9.00 (t, 2 arom. H), 8.97 (t, 4 arom. H), 8.67 (t, 1 arom. H), 8.61 (t, 8 arom. H), 8.42 (d, 4 arom. H), 8.39 (d, 8 arom. H), 8.12 (d, 32 arom. H), 8.10 (d, 16 arom. H), 7.97 (d, 2 arom. H), 7.72 (d, 32 arom. H), 7.65 (d, 32 arom. H), 7.61 (d, 32 arom. H), 7.29 (d, 32 arom. H), 6.95 (d, 32 arom. H), 4.34 (t, 32 H, CO_2CH_2), 4.01 (t, 32 H, CH_2O), 1.9–1.6 (m, 64 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 192 aliph. H), 1.02 (s, 9 H, $(CH_3)_3CSi$), 0.30 (s, 6 H, $(CH_3)_2Si$). Anal. Calcd for $C_{606}H_{572}N_{16}O_{109}Si$ (9851.31): C, 73.89; H, 5.85; N, 2.27%. Found: C, 73.85; H, 6.02; N, 2.21%.

Compound 29. To a solution of **28** (1.34 g, 0.136 mmol) in THF (50 ml) were added $Zn(BF_4)_2$ (0.8 g, 2.2 mmol) and H_2O (3 ml). The mixture was stirred at room temperature for 18 h. Evaporation of THF gave a precipitate which was removed by filtration. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **29** (1.12 g, 85%). $T_c = 256$ °C. ^1H NMR (200 MHz, $CDCl_3$): δ 9.03 (t, 2 arom. H), 9.00 (t, 4 arom. H), 8.64 (t, 8 arom. H), 8.59 (t, 1 arom. H), 8.43 (d, 8 arom. H), 8.42 (d, 4 arom. H), 8.13 (d, 16 arom. H), 8.12 (d, 32 arom. H), 7.97 (d, 2 arom. H), 7.71 (d, 32 arom. H), 7.65 (d, 32 arom. H), 7.61 (d, 32 arom. H), 7.30 (d, 32 arom. H), 6.96 (d, 32 arom. H), 4.36 (t, 32 H, CO_2CH_2), 4.02 (t, 32 CH_2O), 1.9–1.7 (m, 64 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 192 aliph. H). Anal. Calcd for $C_{600}H_{558}N_{16}O_{109}$ (9737.05): C, 74.01; H, 5.78; N, 2.30%. Found: C, 73.92; H, 5.94; N, 2.26%.

Note: for the synthesis of **23**, **26** and **29**, removal of the THF sometimes gave a gummy compound which was difficult to recover by filtration. In such cases, CH_2Cl_2 was added, the organic layer was separated from water, dried ($MgSO_4$), and concentrated to dryness. The solid residue was then purified by CC as described in the procedures.

Compound 30. To a solution of **16** (25 mg, 0.046 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C were added a solution of DPTS (20 mg, 0.068 mmol), DCC (40 mg, 0.194 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **29** (900 mg, 0.092 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5 then 10 : 0.7) gave pure **30** (639 mg, 70%). ^1H NMR (200 MHz, $CDCl_3$): δ 9.02 (t, 4 arom. H), 8.98 (t, 8 arom. H), 8.96 (t, 2 arom. H), 8.62 (t, 16 arom. H), 8.43 (d, 8 arom. H), 8.40 (d, 20 arom. H), 8.13 (d, 68 arom. H), 8.12 (d, 32 arom. H), 7.71 (d, 64 arom. H), 7.65 (d, 64 arom. H), 7.61 (d, 64 arom. H), 7.29 (d, 64 arom. H), 6.95 (d, 68 arom. H), 4.35 (t, 64 H, isoph-CO_2CH_2), 4.15 (t, 4 H, mal-CO_2CH_2), 4.01 (t, 68 H,

CH_2O), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.7 (m, 136 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 392 aliph. H). Anal. Calcd for $C_{1229}H_{1148}N_{32}O_{226}$ (19982.67): C, 73.87; H, 5.79; N, 2.24%. Found: C, 73.88; H, 5.80; N, 2.26%.

Compound 6. To a solution of C_{60} (52 mg, 0.072 mmol) in toluene (100 ml), were added a solution of **30** (481 mg, 0.024 mmol) in CH_2Cl_2 (5 ml), a solution of iodine (6 mg, 0.024 mmol) in toluene (5 ml) and DBU (7 mg, 0.046 mmol). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with CH_2Cl_2–AcOEt 10 : 0.6) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into acetone) gave pure **6** (105 mg, 21%). VIS (λ_{max} in nm (ε in $dm^3\ mol^{-1}\ cm^{-1}$), CH_2Cl_2): 426 (3490), 456 (2300), 687 (190). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.03 (t, 4 arom. H), 8.99 (t, 8 arom. H), 8.96 (t, 2 arom. H), 8.63 (t, 16 arom. H), 8.45 (d, 8 arom. H), 8.41 (d, 20 arom. H), 8.13 (d, 68 arom. H), 8.12 (d, 32 arom. H), 7.71 (d, 64 arom. H), 7.65 (d, 64 arom. H), 7.61 (64 arom. H), 7.30 (d, 64 arom. H), 6.95 (d, 68 arom. H), 4.53 (t, 4 H, $C_{60}CCO_2CH_2$), 4.36 (t, 64 H, isoph-CO_2CH_2), 4.02 (t, 68 H, CH_2O), 1.9–1.6 (m, 136 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.2 (m, 392 aliph. H). Anal. Calcd for $C_{1289}H_{1146}N_{32}O_{226}$ (20701.31): C, 74.79; H, 5.58; N, 2.17%. Found: C, 74.69; H, 5.51; 2.18%.

Compound 33. Ethyl malonyl chloride (**31**) (2.39 g, 15.9 mmol) was added to a suspension of **32** (3.86 g, 16.2 mmol) in CH_2Cl_2 (50 ml). To this mixture was added a solution of Et_3N (1.60 g, 15.8 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.4) gave pure **33** (2.27 g, 41%). $T_m = 88\ ^\circ C$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.22 (br, 1 H, CO_2H), 8.03 (d, 2 arom. H), 6.90 (d, 2 arom. H), 4.18 (m, 2 H, $CO_2CH_2CH_3$), 4.14 (t, 2 H, CO_2CH_2), 3.99 (t, 2 H, CH_2O), 3.36 (s, 2 H, $O_2CCH_2CO_2$), 1.79 (m, 2 H, CH_2CH_2O), 1.67 (m, 2 H, $CO_2CH_2CH_2$), 1.6–1.4 (m, 4 aliph. H), 1.25 (t, 3 H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.85, 166.63, 166.54, 163.44, 132.19, 121.35, 114.02, 67.85, 65.29, 61.40, 41.49, 28.79, 28.23, 25.47, 25.41, 13.92. Anal. Calcd for $C_{18}H_{24}O_7$ (352.38): C, 61.35, H, 6.86%. Found: C, 61.36, H, 7.03%.

Compound 34. To a mixture of **33** (123 mg, 0.349 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C were added a solution of DPTS (70 mg, 0.238 mmol), DCC (180 mg, 0.872 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **20** (380 mg, 0.349 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.25) gave pure **34** (480 mg, 97%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.60 (t, 1 arom. H), 8.15 (d, 6 arom. H), 8.06 (d, 2 arom. H), 7.75 (d, 4 arom. H), 7.68 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.98 (d, 6 arom. H), 4.35 (t, 4 H, isoph-CO_2CH_2), 4.21 (m, 2 H, $CO_2CH_2CH_3$), 4.18 (t, 2 H, mal-CO_2CH_2), 4.08 (t, 2 H, $(CH_2)_5CH_2O$), 4.04 (t, 4 H, $(CH_2)_9CH_2O$), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.6 (m, 12 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 28 aliph. H), 1.29 (t, 3 H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.59, 166.51, 164.96, 164.69, 164.42, 163.66, 163.58, 151.46, 150.96, 144.69, 136.51, 132.52, 132.32, 132.22, 128.21, 127.80, 127.54, 127.21, 122.46, 121.05, 120.69, 118.77, 114.31, 114.25, 110.82, 68.21, 68.00, 65.64, 65.27, 61.40, 41.54, 29.34, 29.29, 29.20, 29.11, 28.96, 28.82, 28.52, 28.26, 25.83, 25.50, 25.44, 13.98. Anal. Calcd for $C_{86}H_{90}N_2O_{17}$ (1423.66): C, 72.56; H, 6.37; N, 1.97%. Found: C, 72.42; H, 6.36; N, 1.95%.

Compound 7. To a solution of C_{60} (300 mg, 0.416 mmol) in toluene (250 ml) were added a solution of **34** (297 mg, 0.209 mmol) in CH_2Cl_2 (5 ml), a solution of iodine (53 mg, 0.209 mmol) in toluene (5 ml) and DBU (64 mg, 0.420 mmol). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with CH_2Cl_2–AcOEt 10 : 0.15) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into acetone) gave pure **7** (269 mg, 60%). VIS (λ_{max} in nm (ε in $dm^3\ mol^{-1}\ cm^{-1}$), CH_2Cl_2): 426 (2680), 486 (1550), 687 (220). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.60 (t, 1 arom. H), 8.15 (d, 4 arom. H), 8.14 (d, 2 arom. H), 8.05 (d, 2 arom. H), 7.75 (d, 4 arom. H), 7.68 (d, 4 arom. H), 7.64 (d, 4 arom. H), 7.33 (d, 4 arom. H), 6.98 (d, 6 arom. H), 4.57 (m, 2 H, $CO_2CH_2CH_3$), 4.54 (t, 2 H, $C_{60}CCO_2CH_2$), 4.36 (t, 4 H, isoph-CO_2CH_2), 4.07 (t, 2 H, CH_2O), 4.04 (t, 4 H, CH_2O), 2.0–1.7 (m, 12 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.49 (t, 3 H, CH_3), 1.6–1.3 (m, 28 aliph. H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.02, 164.76, 164.45, 163.63, 163.52, 151.50, 150.99, 145.30, 145.18, 145.10, 144.80, 144.60, 144.54, 143.79, 143.01, 142.94, 142.87, 142.11, 141.82, 141.79, 140.88, 139.04, 138.80, 136.62, 132.60, 132.43, 132.29, 128.29, 127.91, 127.63, 127.27, 122.52, 121.11, 120.81, 118.82, 114.37, 114.31, 110.90, 71.52, 68.28, 68.00, 67.17, 65.70, 63.39, 52.21, 29.40, 29.36, 29.26, 29.17, 29.02, 28.60, 28.48, 25.90, 25.76, 25.62, 14.24. Anal. Calcd for $C_{146}H_{88}N_2O_{17}$ (2142.30): C, 81.86; H, 4.14; N, 1.31%. Found: C, 81.91; H, 4.32; N, 1.32%.

Compound 35. To a mixture of **33** (83 mg, 0.236 mmol) in CH_2Cl_2 (5 ml) cooled to 0 °C were added a solution of DPTS (40 mg, 0.136 mmol), DCC (126 mg, 0.611 mmol) and 4-PPy (spatula tip) in CH_2Cl_2 (5 ml), and then a solution of **23** (547 mg, 0.235 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2–AcOEt 10 : 0.5) gave pure **35** (625 mg, 100%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.94 (t, 1 arom. H), 8.64 (t, 2 arom. H), 8.36 (d, 2 arom. H), 8.18 (d, 2 arom. H), 8.14 (d, 8 arom. H), 8.12 (d, 4 arom. H), 7.74 (d, 8 arom. H), 7.67 (d, 8 arom. H), 7.63 (d, 8 arom. H), 7.32 (d, 8 arom. H), 7.00 (d, 2 arom. H), 6.97 (d, 8 arom. H), 4.37 (t, 8 H, isoph-CO_2CH_2), 4.21 (m, 2 H, $CO_2CH_2CH_3$), 4.18 (t, 2 H, mal-CO_2CH_2), 4.04 (t, 10 H, CH_2O), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.9–1.6 (m, 20 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.6–1.3 (m, 52 aliph. H), 1.28 (t, 3 H, CH_3). Anal. Calcd for $C_{162}H_{160}N_4O_{31}$ (2659.05): C, 73.18; H, 6.06; N, 2.11%. Found: C, 73.29; H, 6.13; N, 2.10%.

Compound 8. To a solution of C_{60} (190 mg, 0.264 mmol) in toluene (200 ml) were added a solution of **35** (350 mg, 0.132 mmol) in CH_2Cl_2 (5 ml), a solution of iodine (33 mg, 0.130 mmol) in CH_2Cl_2 (5 ml) and DBU (40 mg, 0.263 mmol). The mixture was stirred at room temperature for 18 h, and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C_{60}, and then with CH_2Cl_2–AcOEt 10 : 0.15) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into acetone) gave pure **8** (240 mg, 54%). VIS (λ_{max} in nm (ε in $dm^3\ mol^{-1}\ cm^{-1}$), CH_2Cl_2): 426 (2800), 489 (1630), 687 (210). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.94 (t, 1 arom. H), 8.64 (t, 2 arom. H), 8.35 (d, 2 arom. H), 8.16 (d, 2 arom. H), 8.14 (d, 8 arom. H), 8.12 (d, 4 arom. H), 7.73 (d, 8 arom. H), 7.67 (d, 8 arom. H), 7.62 (d, 8 arom. H), 7.31 (d, 8 arom. H), 6.99 (d, 2 arom. H), 6.97 (d, 8 arom. H), 4.56 (m, 2 H, $CO_2CH_2CH_3$), 4.54 (t, 2 H, $C_{60}CCO_2CH_2$), 4.37 (t, 8 H, isoph-CO_2CH_2), 4.03 (t, 10 H, CH_2O), 2.0–1.6 (m, 20 H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.48 (t, 3 H, CH_3), 1.6–1.3 (m, 52 aliph. H). Anal. Calcd for $C_{222}H_{158}N_4O_{31}$ (3377.70): C, 78.94; H, 4.71; N, 1.66%. Found: C, 79.04; H, 4.81; N, 1.66%.

Acknowledgements

RD acknowledges the Swiss National Science Foundation for financial support (grant no 20-58956.99). The authors thank P. Masson for his help in the molecular simulation studies . The French–Swiss international program of scientific collaboration PICS No. 742 is gratefully acknowledged.

References

1 K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, F. Wudl, G. Srdanov, S. Shi and M. Kao, *J. Am. Chem. Soc.*, 1993, **115**, 9836; C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun*, 1994, 925.
2 M. Brettreich and A. Hirsch, *Tetrahedron Lett.*, 1998, **39**, 2731.
3 F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart and S. Wang, *Langmuir*, 1998, **14**, 1955.
4 A. P. Maierhofer, M. Brettreich, S. Burghardt, O. Vostrowsky, A. Hirsch, S. Langridge and T. M. Bayerl, *Langmuir*, 2000, **16**, 8884.
5 M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl and A. Hirsch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1845.
6 A. Herzog, A. Hirsch and O. Vostrowsky, *Eur. J. Org. Chem.*, 2000, 171; F. Djojo, E. Ravanelli, O. Vostrowsky and A. Hirsch, *Eur. J. Org. Chem.*, 2000, 1051.
7 X. Camps, H. Schönberger and A. Hirsch, *Chem. Eur. J.*, 1997, **3**, 561.
8 X. Camps, E. Dietel, A. Hirsch, S. Pyo, L. Echegoyen, S. Hackbarth and B. Röder, *Chem. Eur. J.*, 1999, **5**, 2362.
9 J.-F. Nierengarten, *Chem. Eur. J.*, 2000, **6**, 3667.
10 J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 1999, **40**, 269; J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 1999, **40**, 273; N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten and V. Vicinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 3730.
11 J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 2000, **41**, 41; D. Felder, H. Nierengarten, J.-P. Gisselbrecht, C. Boudon, E. Leize, J.-F. Nicoud, M. Gross, A. Van Dorsselaer and J.-F. Nierengarten, *New J. Chem.*, 2000, **24**, 687.
12 D. Felder, J.-L. Gallani, D. Guillon, B. Heinrich, J.-F. Nicoud and J.-F. Nierengarten, *Angew. Chem., Int. Ed.*, 2000, **39**, 201.
13 J.-F. Nierengarten, L. Oswald, J.-F. Eckert, J.-F. Nicoud and N. Armaroli, *Tetrahedron Lett.*, 1999, **40**, 5681; M. Numata, A. Ikeda, C. Fukuhara and S. Shinkai, *Tetrahedron Lett.*, 1999, **40**, 6945; J.-F. Eckert, D. Byrne, J.-F. Nicoud, L. Oswald, J.-F. Nierengarten, M. Numata, A. Ikeda, S. Shinkai and N. Armaroli, *New. J. Chem.*, 2000, **24**, 749.
14 C. Bingel, *Chem. Ber.*, 1993, **126**, 1957; J.-P. Bourgeois, F. Diederich, L. Echegoyen and J.-F. Nierengarten, *Helv. Chim. Acta*, 1998, **81**, 1835.
15 T. Chuard and R. Deschenaux, *Helv. Chim. Acta*, 1996, **79**, 736.
16 R. Deschenaux, M. Even and D. Guillon, *Chem. Commun.*, 1998, 537.
17 B. Dardel, R. Deschenaux, M. Even and E. Serrano, *Macromolecules*, 1999, **32**, 5193.
18 T. Chuard, R. Deschenaux, A. Hirsch and H. Schönberger, *Chem. Commun.*, 1999, 2103.
19 S. Campidelli and R. Deschenaux, *Helv. Chim. Acta*, 2001, **84**, 589.
20 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.
21 N. Tirelli, F. Cardullo, T. Habicher, U. W. Suter and F. Diederich, *J. Chem. Soc., Perkin Trans. 2*, 2000, 193.
22 C. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010; C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; J. M. J. Fréchet, *Science*, 1994, **263**, 1710.
23 T. M. Miller, E. W. Kwock and T. X. Neenan, *Macromolecules*, 1992, **25**, 3143.
24 B. C. Ranu, U. Jana and A. Majee, *Tetrahedron Lett.*, 1999, **40**, 1985.
25 S. B. Sastri and S. I. Stupp, *Macromolecules*, 1993, **26**, 5657.
26 B. Ma, C. E. Bunker, R. Guduru, X.-F. Zhang and Y.-P. Sun, *J. Phys. Chem. A*, 1997, **101**, 5626.
27 U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thielgen, P. Uhlmann, A. Vasella, C. A. A. Waldraff and M. Walter, *Chem. Eur. J.*, 1995, **1**, 243.
28 D. Guillon and A. Skoulios, *J. Phys.*, 1976, **37**, 797.
29 F. Hardouin, A.-M. Levelut, M. F. Achard and G. Sigaud, *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80**, 53.
30 J. D. Lister, R. J. Birgeneau, M. Kaplan, C. R. Safinya and J. Als-Nielsen, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, ed. T. Riste, Plenum Press, New York, 1980.
31 D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Eur. J.*, 2000, **6**, 3501.
32 M. Even, B. Heinrich, D. Guillon, D. M. Guldi, M. Prato and R. Deschenaux, *Chem. Eur. J.*, 2001, **7**, 2595.