Liquid-Crystalline Properties of Poly(propylene imine) Dendrimers Functionalized with Cyanobiphenyl Mesogens at the Periphery

Maurice W. P. L. Baars, Serge H. M. Söntjens, Hartmut M. Fischer, H. W. I. Peerlings, and E. W. Meijer*

Abstract: Three generations poly(propylene imine) dendrimers with 4, 16, and 64 terminal amine groups have been functionalized with pentyloxycyanobiphenyl and decyloxycyanobiphenyl mesogens. The liquid-crystalline properties of these dendrimers have been studied in detail by differential scanning calorimetry, optical polarization microscopy, and X-ray diffraction. All the mesogenic dendrimers orient into a smectic A mesophase. Thermal properties are influenced to a large extent by the spacer length, showing g $\rightarrow S_A \rightarrow$ I transitions for the dendritic mesogens with the pentyloxy spacers and K $\rightarrow S_A \rightarrow$ I transitions for the ones with a decyloxy spacer. In the latter, the temperature range of the mesophase increases with dendrimer generation. Mesophase formation in the case of the pentyloxy series is more difficult compared with the corresponding decyloxy analogues, when the transition enthalpies and the kinetics of obtaining microscopic textures are considered. The effect of generation on mesophase formation cannot be clearly distinguished, although in the case of the fifth-generation dendrimer with a decyloxy spacer, microscopic textures could be obtained more easily, compared with the lower generations. X-ray diffraction measurements of oriented samples indicate that the cyanobiphenyl endgroups of both series orient into an antiparallel-overlapping interdigitated structure. The observed S_A-layer spacings are independent of the dendrimer generation for both spacer lengths, indicating that the dendritic backbone has to adopt a completely distorted conformation, even for the higher generations.

Keywords: cyanobiphenyl · dendrimers · distorted conformation · liquid crystals · supramolecular chemistry

Introduction

The use of dendrimers[1–3] as well-defined building blocks with nanometer dimensions for the construction of supramolecular architectures is attracting a great deal of attention. The multifunctional and three-dimensional structure allows the use of dendrimers as large homogeneous catalytic systems,[4] enzyme-mimicing host–guest systems,[2d, 5] or self-assembling modules.[6] The monodisperse character of the dendritic molecules and the shape persistence of their three-dimensional conformation play an important role in these applications.

Recently liquid-crystalline dendrimers have proven to be an interesting new family of (polymeric) mesogenic compounds with dimensions and molecular weights in between low molecular weight mesogens,[7] such as monomeric,[8] dimeric,[9a,b] and oligomeric[9c–f] compounds, and high molecular weight main-chain or side-chain liquid-crystalline polymers.[9g,h] Dendritic properties, like the absence of entanglements and the high local concentration of endgroups, explain the interest in dendritic mesogenic molecules as potential liquid-crystalline materials with an interesting balance in viscosity and thermodynamic stability.

Percec et al.[10] showed that incorporation of rodlike units in hyperbranched polymers[10a] yielded nematic mesophases, whereas the dendritic analogues[10b,c] showed both nematic and smectic mesophases. Kumar and Ramakrishnan[11] showed, however, that in case of random distribution of mesogenic units in a hyperbranched polymer, liquid-crystalline properties were suppressed. Lattermann et al.[12] showed that the coupling of 3,4-bis(decyloxy)benzoyl groups onto a poly(propylene imine) dendrimer skeleton induced shape anisotropy, yielding hexagonal columnar mesophases for the second to fourth generations. In the case of the fifth generation, with 64 endgroups, no mesophase was formed.

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0947-6539/98/0412-2456 $ 17.50+.50/0

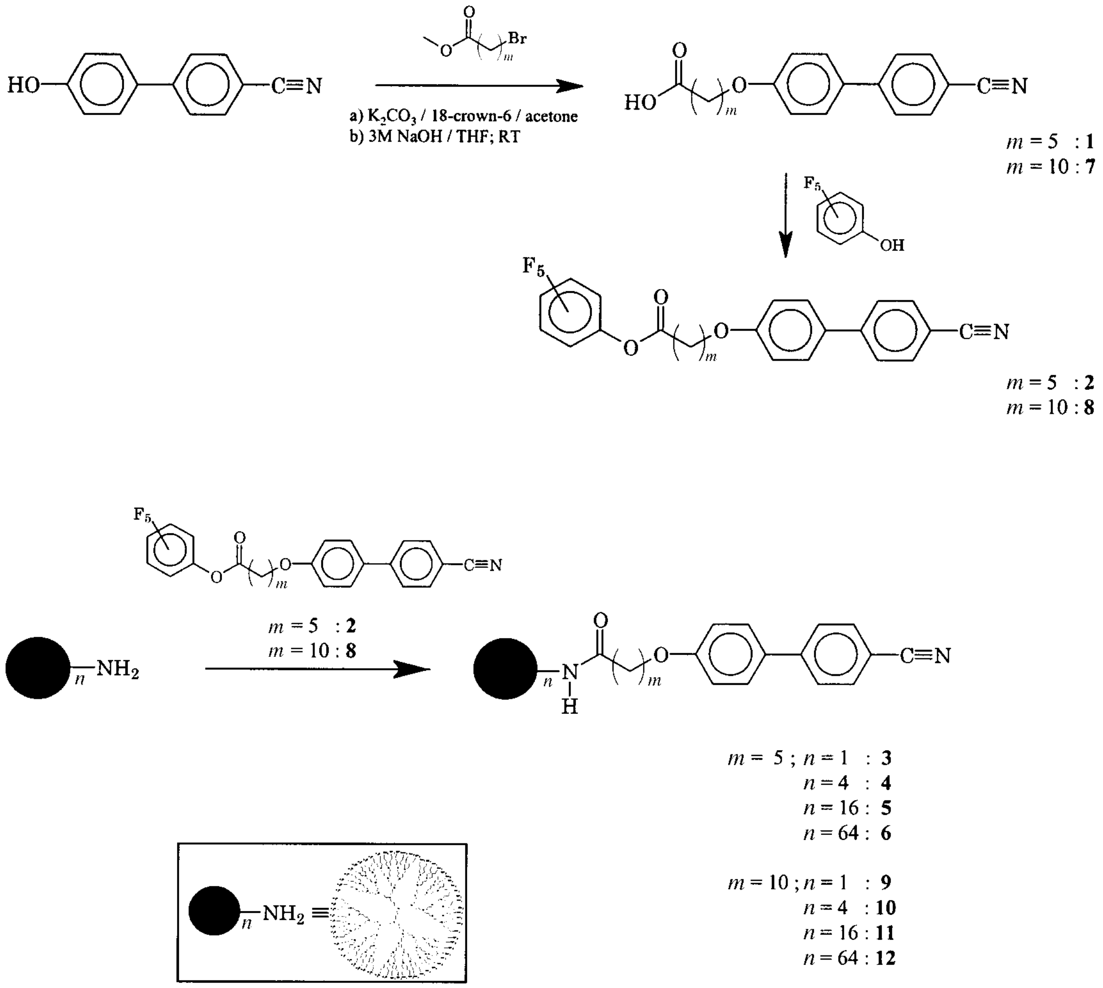
The three-dimensional geometry of a fifth generation is likely to surpress the formation of a columnar structure. Moore et al.[13] observed discotic behavior by attachment of flexible ethylene oxide oligomers to a rigid phenylacetylene core, again as a consequence of molecular-shape anisotropy. Frey et al.[14a] and Shibaev et al.[14b] connected rodlike mesogenic units to the periphery of a multifunctional dendritic carbosilane skeleton; the formation of smectic mesophases was observed. Recently, attention has been paid to the effect of spacer length on liquid-crystalline properties of these mesogenic dendrimers.[15] From all these studies, it is evident that the geometrical requirements to obtain a well-defined mesophase is highly dependent on the (three-dimensional) dendrimer dimensions.

Here we present a study of cyanobiphenyl (CBPh) mesogenic units coupled in a remote way to the periphery of poly(propylene imine) dendrimers, varying both the spacer length of the cyanobiphenyl mesogens and the dimensions (generations) of the dendrimers. These variations enable us to study the effect of molecular structure on the self-assembly of the different dendritic mesogens in the liquid-crystalline mesophase. It is an intriguing question whether a (symmetrical) dendritic skeleton is able to impede liquid-crystalline properties, or whether the high local concentration of mesogenic units in a dendritic molecule leads to pre-organisation and facilitates the formation of a mesophase.

Results and Discussion

Synthesis and characterisation: We have synthesized two series of poly(propylene imine) dendrimers,[3, 16] functionalized with pentyloxy and decyloxy cyanobiphenyl mesogens, denoted as DAB-*dendr*-(NHCO$-$C$_5$$-$CBPh)$_n$ ($n=1$, **3**; $n=4$, **4**; $n=16$, **5**; $n=64$, **6**) and DAB-*dendr*-(NHCO$-$C$_{10}$$-$CBPh)$_n$ ($n=1$, **9**; $n=4$, **10**; $n=16$, **11**; $n=64$, **12**), respectively (Schemes 1a and 1b).

Pentafluorophenyl esters of 6-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]hexanoic acid (**1**) and 11-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]undecanoic acid (**7**)[17] were coupled to different generations of amine-functionalized poly(propylene imine) dendrimers ($n=4$, 16, and 64) and to our model compound *n*-propylamine ($n=1$) with *n* being the number of functional groups. In contrast to the pentafluorophenol derivatives **2** and **8**, the corresponding *N*-hydroxysuccinimidoyl esters[18] proved to be quite unreactive. All dendritic mesogens **3**–**6** and **9**–**12** could be obtained by treating the amine-functionalized dendrimers with a small excess of the pentafluorphenol



Scheme 1. a) Synthesis of functional cyanobiphenyl substituents (**1**, **2**, **7**, and **8**). b) Synthesis of cyanobiphenyl-functionalized poly(propylene imine) dendrimers.

derivatives and followed by precipitation of the dendritic products, which are insoluble in solvents like MeOH or *n*-hexane.

Mass spectrometry (FAB-MS and MALDI-TOF) has been conducted to examine defects within the dendritic structures (incomplete reactions). The amine-functionalized poly(propylene imine) dendrimers, DAB-*dendr*-$(NH_2)_n$ ($n = 4-64$) have been characterized previously by ESI-MS in detail.[19] DAB-*dendr*-$(NH_2)_4$ gives a pure organic compound (96%), while DAB-*dendr*-$(NH_2)_{16}$ contains the pure product (64%) and two defect structures, which can be attributed to dendrimers missing one and two branches, respectively. DAB-*dendr*-$(NH_2)_{64}$ has a (dendritic) purity of approximately 20% and a calculated polydispersity of 1.002. As a consequence a small number of defects will be present in the fifth-generation poly(propylene imine) dendrimer. FAB-MS has been used to characterize the first-generation dendritic mesogens **4** and **10**. The experimental masses ($[M+H]^+$) of 1483 and 1764 amu, were in excellent agreement with the calculated masses for **4** and **10** of 1482.9 and 1763.5 amu, respectively. No defect structures, due to incomplete coupling, could be detected. MALDI-TOF-MS analysis of the third-generation dendrimers **5** and **11** showed a parent peak ($[M+H]^+$) of 6346.7 (calcd 6348.4) and 7449.3 (calcd 7470.5),[20] respectively. No peaks attributed to dendrimers missing one mesogenic unit were detected, indicating that all primary amine endgroups were modified.[21] The defects that were found, originate from defects in the starting material. It proved to be impossible to analyze the fifth-generation dendrimers with MALDI-TOF-MS, despite variations in the experimental conditions. This is probably due the high molar mass (30000 amu), thus leading to difficulties in achieving a considerable amount of ionization in the case of dendrimers **6** and **12**.

All NMR (^1H and ^{13}C) and IR spectroscopic data of compounds **1**–**12** are in full agreement with the structures proposed. The properties of the functionalized dendrimers were studied in detail by means of differential scanning calorimetry (DSC), polarization microscopy, and X-ray diffraction.

Differential scanning calorimetry: The phase transitions of the pentyloxy-substituted compounds **3**–**6** and decyloxy-substituted compounds **9**–**12**, have been studied with DSC, with heating and cooling rates of 10 K min^{-1}. All samples were dried in a vacuum oven prior to analysis.

All dendrimers with a pentyl spacer, **4**–**6**, show liquid-crystalline behavior. DSC traces of these dendrimers are depicted in Figure 1.[22] Phase transition temperatures and thermodynamic data of compounds **3**–**6** and reference compound C_5–CBPh[23] are summarized in Table 1.

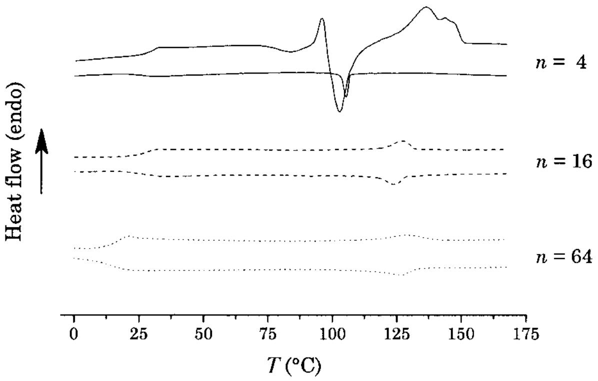


Figure 1. DSC traces of DAB-*dendr*-(NHCO–C_5–CBPh)$_n$ ($n = 4$, 16, and 64); first cooling run (lower trace), second heating run (upper trace).

Table 1. Transition temperatures and thermal data[a] for DAB-*dendr*-(NHCO–C_5–CBPh)$_n$

	g		K		M		I
C_5–BPh			•	50 (86; *23*)	•	68 (1.8; *0.5*)	•
$n = 1$ (**3**)			•	119 (69; *23*)			•
$n = 4$ (**4**)	•	31 (0.79; *0.29*)	•	155[b] (–)	•	{106}[c] (4.8; *1.8*)	•
$n = 16$ (**5**)	•	25 (0.49; *0.19*)			•	127 (4.9; *2.0*)	•
$n = 64$ (**6**)	•	13 (0.37; *0.15*)			•	129 (3.6; *1.5*)	•

[a] Glass transitions are depicted in J g^{-1}K^{-1} or *kJ mol^{-1} K^{-1}*, all other transitions in J g^{-1} or *kJ mol^{-1}* [b] Broad (re)crystallization trajectory from 75–155 °C (see Figure 2), melting at 155 °C. [c] Compound **10** shows liquid-crystalline behavior upon cooling from the isotropic state.

Propylamine derivative **3** remains crystalline up to complete melting and does not show the formation of a liquid-crystalline mesophase. In the case of the higher generations ($n = 16$ and 64), a broad mesophase is observed in between the glass transition and the clearing point. Upon heating, the first-generation also shows a transition from the glassy state into the mesophase, but starts to recrystallize above 75 °C and becomes isotropic at 155 °C. This type of complex melting behavior is commonly observed for first-generation substituted poly(propylene imine) dendrimers;[24] this is attributed to both inter- and intramolecular hydrogen-bond interactions. Even at low cooling rates (1, 2, or 5 K min^{-1}) the thermogram remained unchanged and crystallization did not occur. These results indicate that the branched topology strongly impedes crystallization. Dendritic mesogens with a pentyloxy spacer resemble side-chain liquid-crystalline polymers with a short spacer between the mesogenic unit and the dendritic scaffold,[9g–h, 25a–b] yielding liquid-crystalline behavior in between the glassy state and isotropic liquid. The observed results also agree with observations for cyanobiphenyl functionalized carbosilane dendrimers with a short spacer.[14a]

The enthalpy of the transition from mesophase into isotropic liquid for compounds **4**–**6** in all cases amounts to 4–5 J g^{-1} (1.5–2.0 kJ mol^{-1}), which hints at a smectic→isotropic transition. Expression of the enthalpy in kJ mol^{-1} reflects the transition energy per mesogenic unit in the dendrimer and demonstrates an almost generation independent behavior.

The dendrimers with a decyloxy spacer (**10**, **11**, and **12**) also show liquid-crystalline behavior for all generations. DSC traces of dendrimers **10**–**12** are depicted in Figure 2.[22] Phase-transition temperatures and thermodynamic data of compounds **9**–**12** and reference compound 4-(decyloxy)-4′-cyanobiphenyl (C_{10}–CBPh)[23] are summarized in Table 2.

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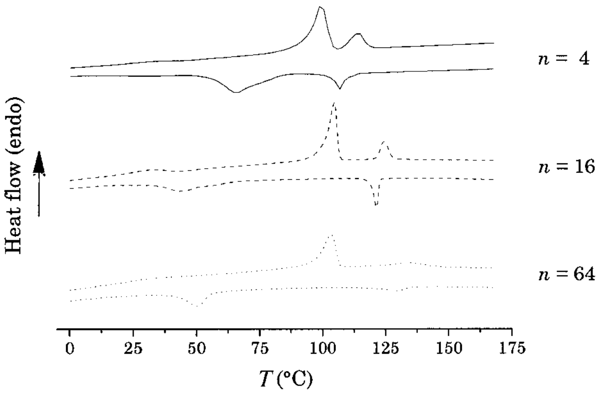

Figure 2. DSC traces of dendrimers DAB-*dendr*-(NHCO–C_{10}–CBPh)$_n$ (n = 4, 16, and 64); first cooling run (lower trace), second heating run (upper trace).

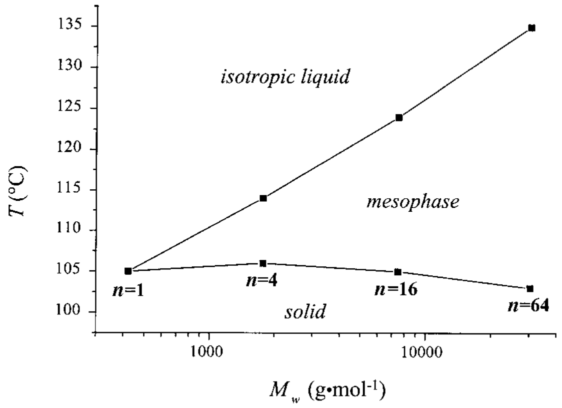

Figure 3. Transition temperatures of cyanobiphenyl dendrimers with a decyl spacer, that is, DAB-*dendr*-(NHCO–C_{10}–CBPh)$_n$, as a function of molecular weight.

Table 2. Transition temperatures and thermal data[a] for DAB-*dendr*-(NHCO–C_{10}–CBPh)$_n$

	g[b]		K		M		I
C_{10}–CBPh			•	59 (98; *33*)	•	86 (7.8; *2.6*)	•
n = 1 (**9**)			•	105 (84; *34*)			•
n = 4 (**10**)	•	22 (–)	•	106 (34; *15*)	•	114 (9.2; *4.0*)	•
n = 16 (**11**)	•	26 (–)	•	105 (37; *17*)	•	124 (8.8; *4.1*)	•
n = 64 (**12**)	•	22 (–)	•	103 (32; *15*)	•	135 (8.7; *4.1*)	•

[a] Glass transitions are depicted in $J\,g^{-1}K^{-1}$ or *kJmol*$^{-1}$*K*$^{-1}$, all other transitions in $J\,g^{-1}$ or *kJmol*$^{-1}$ [b] Dendrimers **10**–**12** show small glass transitions that were hardly visible; thermal data were not determined.

Propylamine derivative **9** remains crystalline up to complete melting, but does not show a liquid-crystalline mesophase. Hydrogen bonding of the amide residue in the melt is likely to account for this behavior. In the case of dendrimers **10**–**12**, upon cooling from the isotropic liquid, a mesophase is entered before a transition into the semi-crystalline state. A (small) glass transition can be detected at lower temperature. Hydrogen bonding is also likely to account for the substantially higher transition temperatures of the dendritic compounds in comparison with C_{10}–CBPh (Table 2).

The phase-transition temperatures of the mesogenic dendrimers with a decyl spacer are presented in Figure 3 and show a slight decrease in melting temperature (T_m) and a distinct increase in clearing point (T_c) as a function of dendrimer generation (molecular weight). This stabilisation of the liquid-crystal (LC) phase[8b, 26] can be understood from the restriction of transitional and rotational motion of the mesogenic molecules when linked to the dendritic scaffold.

The transition enthalpy of mesophase to isotropic liquid amounts to 8–9 $J\,g^{-1}$ (4.0 $kJ\,mol^{-1}$) for compounds **10**–**12,** which is of the same order of magnitude as that of the reference compound. Identical transition enthalpies for dendrimers **10**–**12**, expressed in $kJ\,mol^{-1}$, indicate that no distinct effect of generation can be observed, except for the peak transitions that broaden for the higher generations. A detailed study of the broadening of peak transitions in side-chain liquid-crystalline polymers by Pugh et al.[27] revealed that the observed broadening of the peak transitions for the higher generations is not only due to an increase in polydispersity of the dendritic compound, but can also be explained in terms of different microdomains that are present in the liquid-crystalline sample.[27] The transition enthalpies from the crystalline phase to the mesophase are of the same order of magnitude for dendritic compounds **10**–**12**, which suggests that crystallization of the mesogenic units is comparable for the different generations and independent of the (dimensions of the) dendritic skeleton. Dendritic mesogens with a decyloxy spacer show a behavior that is characteristic of a well-defined monodisperse polymer[28] in which the mesogenic unit is (almost) completely decoupled from the dendritic skeleton.

Comparison of the series with pentyloxy and decyloxy spacers reveals that the length of the spacer has a major influence on thermal properties. Recently, similar trends have been observed by Frey et al.[15] The longer the spacer, the more decoupled is the mesogenic unit from the dendritic skeleton. From the DSC traces and the transition enthalpies, we can conclude that the mesophase formation is independent of the dendrimer generation. This is in contrast to the general idea[15] that a larger dendrimer distorts liquid crystallinity to a higher extent and to the observations of Lattermann.[12] In the latter case, the three-dimensional conformation of a fifth-generation poly(propylene imine) dendrimer could not adapt to the requirements of the 3,4-bis(decyloxy)benzoyl substituents attached to the core without spacers.

Polarization microscopy: In order to study the mesophase of the compounds with polarisation microscopy, samples of dendrimers **4**–**6** and **10**–**12** were prepared between glass slides. Upon heating, compound **4** shows a broad melting/recrystallization trajectory, in good agreement with the DSC trace. Upon cooling from the isotropic liquid (I), a mesophase (M) was formed at approximately 110 °C. The structure of the mesophase is converted into a glassy state (g) without any macroscopically recognizable changes. The higher generations showed similar cooling runs, an I → M transition at approximately 130 °C and a M → g transition at room temperature, whereas heating runs showed the reverse behavior, g → M → I. The observed results indicate liquid-crystalline behavior for the glass to isotropic liquid transition[14a] and are in good agreement with the DSC data. Formation of bâtonettes[7a] suggested a smectic A mesophase. Typical textures for compounds **4**–**6** were grown by slowly cooling the isotropic liquid (0.5 K min^{-1}), an example is presented in Figure 4 (top) for a sample of compound **6**. It can clearly be seen from the image that the optical textures grown were very small and initially yielded formation of bâtonettes. Further growth into larger domains proved to be impossible, even after annealing for longer periods. The majority of the image consisted of confocal textures, representing small birefringent regions that were 10 µm in size.

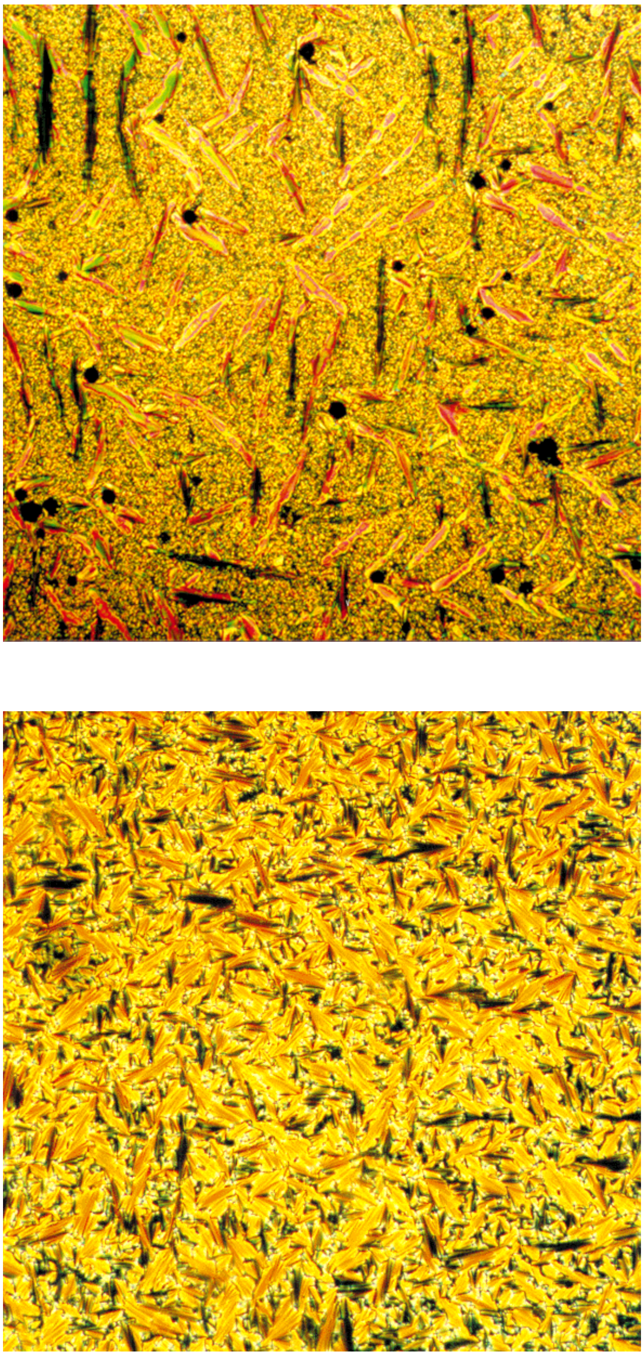
Figure 4. Top: Optical texture of **6** at 120 °C (crossed polarizers, enlargement 200 ×); bottom: Optical texture of **12** at 130 °C (crossed polarizers, enlargement 200 ×).

Compounds **10**–**12** showed the formation of mesophases, in good agreement with the DSC traces. At approximately 105 °C a transition from the semi-crystalline state into the mesophase takes place followed by a transition into the isotropic liquid at higher temperature. Again, typical textures could be grown by slowly cooling the isotropic liquid (1 K min^{-1}). A focal-conic fan-shaped texture,[7a] indicative of a smectic A phase is depicted for compound **12** (Figure 4, bottom). The fast reappearance of the liquid-crystalline phase at 130 °C upon cooling from the isotropic liquid, indicated a high degree of preorientation in the isotropic state, an effect which might be related to the high local concentration of the endgroups in the dendritic structure. Surprisingly, the highest generation gave the best results in growing these focal-conic fan structures. This suggested a tighter packing of the mesogens in the case of the higher generations.

X-ray diffraction: The structures of the mesophases of compounds **4**–**6** and **10**–**12** were examined in detail by X-ray diffraction. Figure 5 shows a flat-camera photograph of oriented samples of **6** and **11** at room temperature obtained by quickly cooling from the mesophase. The X-ray diffraction curves of **11** and **12** are depicted in Figure 6.

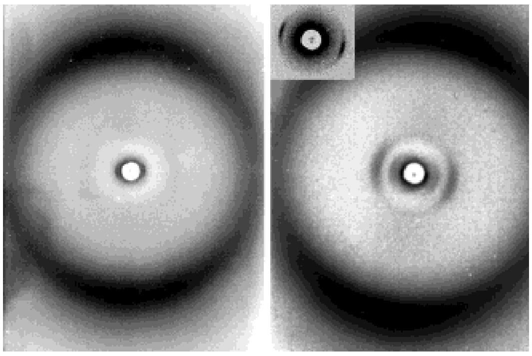
Figure 5. X-ray diffraction pattern of oriented samples of **6** left) and **11** (right) at room temperature. Left: First-order reflections of **6** are located in the beam stop; right: First-, second-, and third-order reflections of **11**. The first-order reflections are located in beam stop, but the inset shows reflections at small angles.

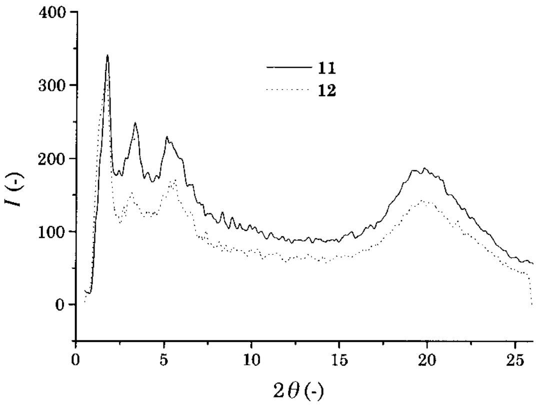

Figure 6. X-ray diffraction curves of **11** (—) and **12** (⋯).

For all mesogenic dendrimers a diffuse wide-angle reflection at 4.4 ± 0.1 Å was observed (Table 3), which is typical for the lateral distance between the mesogens. These values are in agreement with literature data on side-chain polymers containing cyanobiphenyl mesogens.[7a,b] The diffuse nature of the reflection indicates the short-range order of the mesogens. X-ray diffraction patterns of compounds **4**, **5**, and **6** show sharp small-angle reflections (first order) at 36, 39, and 38 Å (Table 3), respectively. These reflections are typical for a smectic A mesophase and indicate a defined packing of the dendritic mesogens in layers. Compounds **10**, **11,** and **12**, with a decyloxy spacer, show small-angle reflections at 45, 44, and 45 Å (Table 3), respectively. Besides sharp, first-order, point-like meridian reflections, second and third order reflections are also observed. The observation of higher order reflections is indicative of a long-range longitudinal order and suggests that the packing of the mesogenic dendrimers with a decyl spacer into smectic layers is more defined than the packing of the pentyl series, in which the higher order reflections are not observed.

Table 3. X-ray diffraction data obtained for DAB-*dendr*-(NHCO−C_m−CBPh)$_n$.

			d-spacings [Å]	
$m=5$	$n=4$	(**4**)	4.4 ± 0.1	36 ± 2
	$n=16$	(**5**)	4.4 ± 0.1	39 ± 2
	$n=64$	(**6**)	4.4 ± 0.1	38 ± 2
$m=10$	$n=4$	(**10**)	4.4 ± 0.1	45 ± 2[a]
	$n=16$	(**11**)	4.4 ± 0.1	44 ± 2[a]
	$n=64$	(**12**)	4.4 ± 0.1	45 ± 2[a]

[a] Spacings are obtained by averaging first-, second-, and third-order reflections.

The formation of smectic mesophases can be explained by a phase separation between the anisometric rigid units and the flexible skeleton (alkyl spacer and dendritic interior) in combination with a microphase separation between the polar dendritic interior and the apolar mesogenic endgroups. The arrangement of the mesogenic endgroups is predominantly perpendicular with respect to the plane of the smectic layer, in which the dendritic backbone is positioned. The mesophase consists of consecutive layers in which the mesogenic units and the dendritic interior are separated. It is known that cyanobiphenyl mesogens, because of their large dipole moment, preferentially orient into an antiparallel-overlapping interdigitated structure.[7a,b] The spacings of the smectic layers are (almost) independent of the dendrimer generation, but are dependent on the spacer length of the mesogenic unit. The constant value of the layer spacings indicates that the dendrimer, for all generations, occupies the same thickness in the smectic layers and that the dendritic interior has to adopt a highly distorted conformation for the higher generations. A proposed model is represented in Figure 7a. It is difficult however to determine the exact degree of overlap of the cyanobiphenyl units and deformation of the flexible skeleton.[9g] Two possible (extreme) cases of overlap are depicted in Figure 7b. An extended decyloxycyanobiphenyl chain occupies a length of 25 Å. To account for the observed layer spacings of approximately 45 Å and the thickness of the dendrimer layer, the cyanobiphenyl parts (of different dendritic molecules) need to have a considerable overlap. Assuming that this overlap is generation independent, a constant dendrimer thickness seems likely, since for all dendrimer generations the volume per endgroup is roughly constant. Currently, experiments are performed to obtain more detailed information about the liquid-crystalline organisation on a molecular scale.

The spontaneous orientation of the mesogenic units forces the (three dimensional) dendritic skeleton into a highly distorted conformation, an observation which is quite common for side-chain liquid-crystalline polymers.[25] Recently similar results have been obtained for poly(propylene imine) dendrimers modified with an apolar periphery of palmitoyl chains.[6d] X-ray measurements of aggregates of the these dendrimers in aqueous media showed bilayer spacings that were roughly generation independent; this indicates that the dendritic interior, for all generations, occupies the same thickness and has to adopt a highly distorted conformation in case of the higher generations.

The observation that, even for the short spacer, well-defined mesophases can be obtained suggests that the polar poly(propylene imine) interior stabilizes the mesophase (strong phase separation). In contrast, the formation of smectic mesophases is less pronounced if an apolar dendritic scaffold is used as a core for mesogenic endgroups.[15]

Conclusions

Amine-functionalized poly(propylene imine) dendrimers have successfully been treated with pentafluorophenyl esters of alkoxycyanobiphenyl mesogens at the periphery of the dendrimer. Three different generations of mesogenic dendrimers have been synthesized with 4, 16, and 64 endgroups, respectively. The spacer between the mesogenic unit and the dendritic core was varied, that is, pentyl or decyl. Differential scanning calorimetry, polarization microscopy, and X-ray investigations indicate the formation of smectic A mesophases for all generations of dendrimers. This is in contrast with observations of other mesogenic poly(propylene imine) dendrimers and the general idea that for the higher generations liquid crystallinity is less readily observed. The cyanobiphenyl dendrimers orient into an antiparallel arrangement, yielding an interdigitated bilayer. The layer spacings obtained from the X-ray investigations are generation independent, both for the mesogenic dendrimers with a decyloxy spacer and a pentyloxy spacer; this suggests that the dendrimer adopts a completely distorted conformation, even in the case of the higher generations. The mesophase formation in the case of the pentyloxy series is more complex than in the decyloxy series, because the latter possesses mesogenic units that are more decoupled from the dendritic skeleton.

The results obtained from this study indicate that under the influence of external stimuli (endgroups) the poly(propylene imine) interior has to undergo significant changes in the conformation and that the flexibility of functionalized poly-

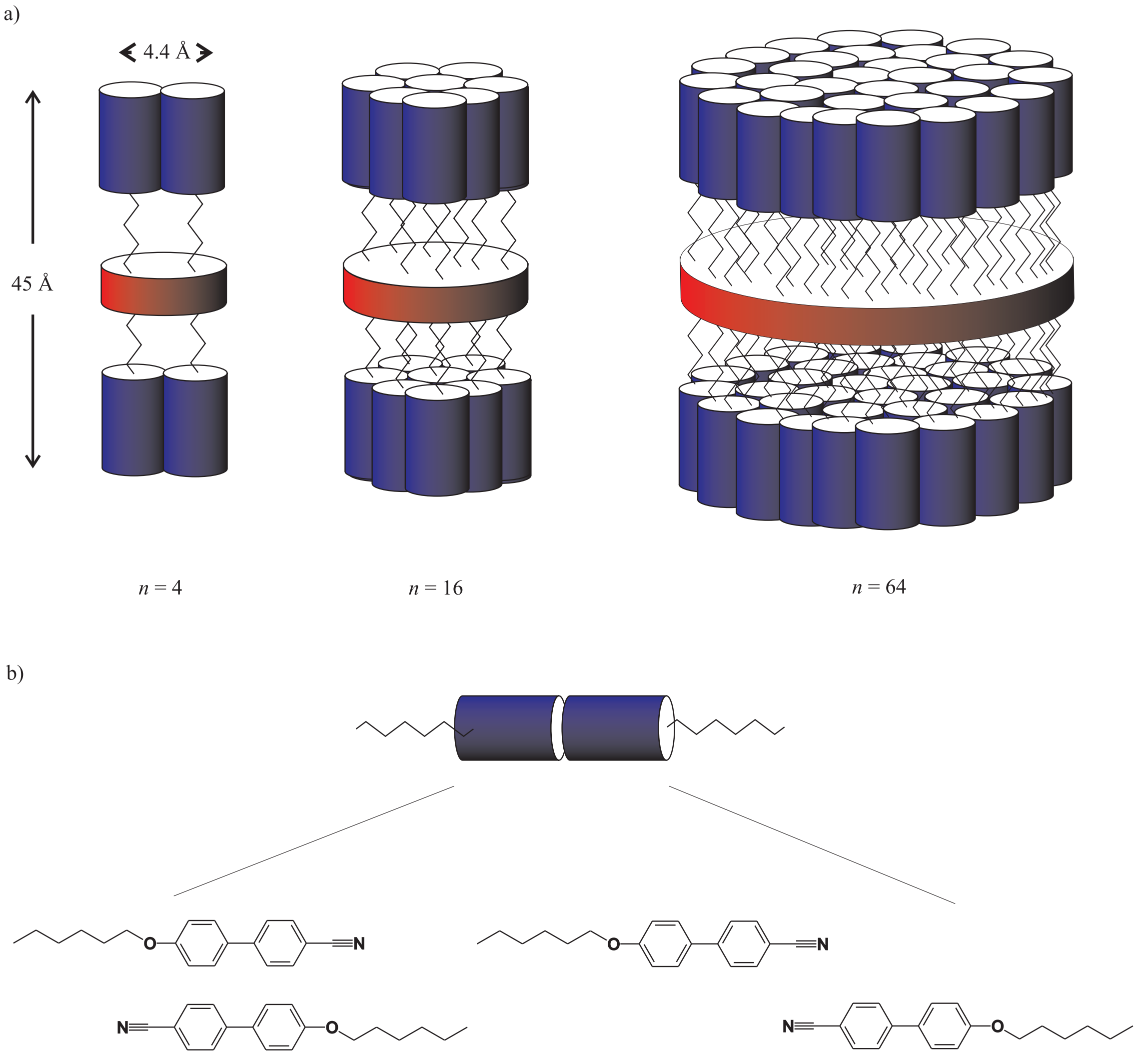

Figure 7. a) Proposed model for the organization of mesogenic dendrimers into smectic layered mesophases, depicted for the first ($n = 4$), third ($n = 16$), and fifth-generation ($n = 64$). Dimensions are shown for the dendrimers with a decyl spacer. b) Detailed representation of possible overlap of the mesogenic fragments in the smectic layers.

(propylene imine) dendrimers, and of functionalized dendrimers in general, is much higher than previously anticipated.

Experimental Section

General: All solvents were of p.a. quality and used as received. 4′-Cyano-4-hydroxybiphenyl (TCI, 98%) and 4′-cyano-4-pentyloxybiphenyl (Aldrich, 99%), 6-bromohexanoic acid (Acros, 98%), 11-undecanoic acid (Acros, 99+ %) were used as received. 4′-Cyano-4-decyloxybiphenyl (99%) was synthesized by etherification of 4′-cyano-4-hydroxybiphenyl and decylbromide, analogous to literature procedures.[29] Synthesis of the methyl esters of 6-bromohexanoic acid and 11-bromoundecanoic acid was performed with an acid-catalyzed esterification in MeOH. Poly(propylene imine) dendrimers with amine endgroups were supplied by DSM Research (The Netherlands). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer at 400.13 MHz and 100.62 MHz respectively, unless noted otherwise. All δ values are given with reference TMS as an internal standard. IR samples were prepared according the KBr technique and were measured on a Perkin–Elmer 1605 Series FT machine. Elemental analysis were performed on a Perkin–Elmer 2400 Series CHNS/O analyzer. Fast atom bombardment mass spectrometry (FAB-MS) was performed at the University of Copenhagen (Denmark). Matrix-assisted laser-desorption ionization/time-of-flight mass spectra (MALDI-TOF-MS) spectra of **5** and **11** were recorded on a Voyager-DE mass spectrometer with α-cyano-4-hydroxycinnamic acid as a matrix (University of California, Berkeley, USA). Thermographic analyses (TGA) were performed on a Perkin–Elmer TGA7 machine to determine thermal stability of the samples. Thermal transitions of compounds **2**–**7** and **9**–**12** were determined by differential scanning calorimetry on a Perkin–Elmer DSC7 or a Perkin–Elmer Pyris 1 under a nitrogen atmosphere with heating and cooling rates of 10 K min^{-1} unless otherwise noted. The optical properties were studied with a Jenaval polarisation microscope equipped with a Linkam THMS 600 heating device, with crossed polarizers. X-ray diffraction patterns of oriented and nonoriented samples were recorded with a flat-film camera at room temperature (Ni filtered, Cu$_{K\alpha}$ radiation ($\lambda = 1.542$ Å).

6-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]hexanoic acid (1):[30] A mixture of 18-crown-6 (0.51 g, 2 mmol), finely ground potassium carbonate (6.5 g, 47 mmol), 4′-cyano-4-hydroxybiphenyl (5.02 g, 25.7 mmol), and methyl-6-bromohexanoate (7.05 g, 33.7 mmol) in acetone (80 mL) was stirred vigorously and heated under reflux for 16 h. The mixture was concentrated in vacuo and recrystallized from MeOH yielding methyl-6-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]hexanoate (7.90 g, 95%) as a white solid. M.p. 127.2 °C; ^{1}H NMR (CDCl$_3$): $\delta = 7.69$ (d, $J = 8.1$ Hz, 2H; H-3′), 7.64 (d, $J = 8.2$ Hz, 2H; H-2′), 7.53 (d, $J = 8.9$ Hz, 2H; H-2), 6.98 (d, $J = 8.8$ Hz, 2H; H-3), 4.02 (t, 2H; CH$_2$CH_2O), 3.69 (s, 3H; COOCH_3), 2.37 (t, 2H; CH$_2$CH_2COO), 1.84 (m, 2H; C$_2$CH$_2$O), 1.73 (m, 2H; CH_2CH$_2$COO), 1.53 (m, 2H;

$\mathit{CH}_2\mathrm{CH_2CH_2O}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 174.3$ ($\mathrm{CH_2}\mathit{C}\mathrm{OO}$), 159.9 (C-4), 145.5 (C-1′), 132.6 (C-3′), 131.8 (C-1), 128.3 (C-2), 127.1 (C-2′), 119.1 (CN), 115.1 (C-3), 108.8 (C-4′), 67.8 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 51.5 ($\mathrm{COO}\mathit{C}\mathrm{H_3}$), 34.0 ($\mathit{C}\mathrm{H_2COO}$), 28.9, 25.6, 24.7 ($(\mathit{C}\mathrm{H_2})_3$); IR (KBr): $\tilde{\nu} = 2946$ ($\mathrm{CH_2}$), 2221 ($\mathrm{C{\equiv}N}$), 1721 cm^{-1} ($\mathrm{C{=}O}$). This ester (6.47 g, 20 mmol) was added to a sodium hydroxide solution (100 mL, 3 M). THF (ca. 15 mL) was then added until a homogeneous suspension was formed. The reaction mixture was stirred at room temperature for 4 days, during which the reaction was monitored with TLC. On complete hydrolysis, the suspension was neutralized with a solution of hydrochloric acid (ca. 5 M) at 0 °C. This furnished the crude product as a white precipitate, which was filtered off and washed with diethylether and water. The crude material was recrystallized twice from EtOH to yield pure acid **1** (4.72 g, 60 %) as white needles. M.p. 89.5 °C; ^{1}H NMR ($\mathrm{CD_3OD}$): $\delta = 12.04$ (br s, 1 H; $\mathrm{CH_2COO}\mathit{H}$), 7.86 (d, $J = 8.4$ Hz, 2 H; H-3′), 7.82 (d, $J = 8.4$ Hz, 2 H; H-2′), 7.68 (d, $J = 8.7$ Hz, 2 H; H-2), 7.03 (d, $J = 8.7$ Hz, 2 H; H-3), 4.00 (t, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 2.23 (t, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{COO}$), 1.73 (m, 2 H; $\mathit{CH}_2\mathrm{CH_2O}$), 1.56 (m, 2 H; $\mathit{CH}_2\mathrm{CH_2COO}$), 1.43 (m, 2 H; $\mathit{CH}_2\mathrm{CH_2CH_2O}$); ^{13}C NMR ($\mathrm{CD_3OD}$): $\delta = 174.5$ ($\mathrm{CH_2}\mathit{C}\mathrm{OO}$), 159.3 (C-4), 144.3 (C-1′), 132.8 (C-3′), 130.3 (C-1), 128.3 (C-2), 126.8 (C-2′), 119.0 (CN), 115.1 (C-3), 109.1 (C-4′), 67.5 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 33.6 ($\mathit{C}\mathrm{H_2COO}$), 28.4, 25.2, 24.3 ($(\mathit{C}\mathrm{H_2})_3$); IR (KBr): $\tilde{\nu} = 3449$ (O–H), 2938 ($\mathrm{CH_2}$), 2227 ($\mathrm{C{\equiv}N}$), 1702 cm^{-1} ($\mathrm{C{=}O}$); $\mathrm{C_{19}H_{19}NO_3}$ (309.36): calcd C 73.76, H 6.19, N 4.53; found C 73.8, H 6.3, N 4.5.

Pentafluorophenyl-6-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]hexanoate (**2**): A solution of acid **1** (4.10 g, 13.3 mmol) and pentafluorophenol (2.98 g, 14.3 mmol) was prepared in dry DMF (100 mL). The homogeneous solution was cooled at 0 °C and DCC (2.72 g, 13.3 mmol) in DMF (2 mL) was added in portions. After complete addition of DCC, the temperature of the reaction mixture was allowed to equilibrate to room temperature. After 4 days the reaction mixture was filtered, and the filtrate was concentrated in vacuo. The product was recrystallized from EtOH to yield crude **2** (5.16 g, 84 %) as a crystalline solid (purity >95 % from ^{1}H NMR). Additional column chromatography ($\mathrm{SiO_2}$: heptane/$\mathrm{CHCl_3}$, 35:65, $R_f = 0.36$) yielded pure **2** (3.69 g, 60 %) as a white solid. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.69$ (d, $J = 8.2$ Hz, 2 H; H-3′), 7.64 (d, $J = 8.2$ Hz, 2 H; H-2′), 7.55 (d, $J = 8.8$ Hz, 2 H; H-2), 6.99 (d, $J = 8.8$ Hz, 2 H; H-3), 4.04 (t, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 2.73 (t, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{COO}$), 1.88 (m, 4 H; $\mathrm{OCH_2}\mathit{CH}_2\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2COO}$), 1.64 (m, 2 H; $\mathrm{OCH_2CH_2}\mathit{CH}_2\mathrm{CH_2CH_2COO}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 169.9$ ($\mathrm{CH_2}\mathit{C}\mathrm{OO}$), 160.2 (C-4), 145.8 (C-1′), 133.1 (C-3′), 132.0 (C-1), 128.9 (C-2), 127.6 (C-2′), 119.6 (CN), 115.6 (C-3), 110.7 (C-4′), 68.2 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 33.8 ($\mathit{C}\mathrm{H_2COO}$), 29.4, 26.0, 25.1 ($(\mathit{C}\mathrm{H_2})_3$); IR (KBr): $\tilde{\nu} = 2878$ ($\mathrm{CH_2}$), 2224 ($\mathrm{C{\equiv}N}$), 1795 cm^{-1} ($\mathrm{C{=}O}$); $\mathrm{C_{25}H_{18}F_5NO_3}$ (475.42): calcd C 63.16, H 3.82, N 2.95; found: C 63.2, H 3.8, N 2.9.

Propyl-NHCO–C$_5$–OCBPh (**3**): *n*-Propylamine (0.2 g, 3.4 mmol) was slowly added to a solution of activated ester **2** (1.00 g, 2.10 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL). After stirring for 1 day, the solution was diluted with $\mathrm{CH_2Cl_2}$ and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was extracted with $\mathrm{CH_2Cl_2}$. The combined organic phases were then washed with demineralized water, dried with sodium sulphate, and concentrated in vacuo yielding pure **3** (660 mg, 90 %) as a white solid. M.p. 119; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.69$ (d, $J = 8.5$ Hz, 2 H; H-3′), 7.63 (d, $J = 8.5$ Hz, 2 H; H-2′), 7.52 (d, $J = 8.8$ Hz, 2 H; H-2), 6.99 (d, $J = 8.8$ Hz, 2 H; H-3), 5.43 (br s, 1 H; $\mathrm{N}\mathit{H}\mathrm{CO}$), 4.01 (t, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 3.22 (q, 2 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{NHCO}$), 2.21 (t, 2 H; $\mathrm{NHCO}\mathit{CH}_2\mathrm{CH_2}$), 1.84 (m, 2 H; $\mathit{CH}_2\mathrm{CH_2O}$), 1.73 (m, 2 H; $\mathrm{NHCOCH_2}\mathit{CH}_2$), 1.53 (m, 4 H; $\mathit{CH}_2\mathrm{CH_2NHCO}$ and $\mathit{CH}_2\mathrm{CH_2CH_2O}$), 0.93 (t, 3 H; $\mathit{CH}_3\mathrm{CH_2CH_2NHCO}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 172.7$ ($\mathrm{CH_2}\mathit{C}\mathrm{ONH}$), 159.7 (C-4), 145.2 (C-1′), 132.5 (C-3′), 131.3 (C-1), 128.3 (C-2), 127.1 (C-2′), 119.1 (CN), 115.0 (C-3), 110.0 (C-4′), 67.8 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 41.2 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2NH}$), 36.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CO}$), 29.0, 25.8, 25.5 ($(\mathit{C}\mathrm{H_2})_3$), 22.9 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2NHCO}$), 11.3 ($\mathit{C}\mathrm{H_3CH_2CH_2NHCO}$); IR (KBr): $\tilde{\nu} = 2990$ ($\mathrm{CH_2}$), 2222 ($\mathrm{C{\equiv}N}$), 1635 cm^{-1} ($\mathrm{C{=}O}$); FAB-MS: *m/z*: 351 $[M+\mathrm{H}]^+$; calcd $\mathrm{C_{22}H_{25}N_2O_2}$ 349.45.

DAB-*dendr*-(NHCO–C$_5$–CBPh)$_4$ (**4**): A solution of DAB-*dendr*-$(\mathrm{NH_2})_4$ (157.3 mg, 0.497 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) was added slowly to a solution of activated ester **2** (1.00 g, 2.10 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL). After stirring for 3 days, the solution was diluted with $\mathrm{CH_2Cl_2}$ and MeOH, and extracted with a saturated sodium carbonate solution. The aqueous phase was extracted with $\mathrm{CH_2Cl_2}$. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in $\mathrm{CH_2Cl_2}$ and precipitated by slowly adding *n*-heptane. The precipitate was dissolved in $\mathrm{CH_2Cl_2}$, washed with demineralized water and dried over sodium sulphate, yielding pure **4** (250 mg, 34 %) as a yellow solid. g 31 °C (M 106 °C) 155 °C I; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.67$ (d, $J = 6.5$ Hz, 8 H; H-3′), 7.61 (d, $J = 6.5$ Hz, 8 H; H-2′), 7.50 (d, $J = 8.8$ Hz, 8 H; H-2), 6.95 (d, $J = 8.8$ Hz, 8 H; H-3), 6.51 (t, 4 H; $\mathrm{CH_2N}\mathit{H}\mathrm{COCH_2}$), 3.97 (t, 8 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 3.29 (q, 8 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{NH}$), 2.40 (t, 8 H; $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_2NH}$), 2.35 (br s, 4 H; $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_2}\mathit{CH}_2\mathrm{N}$), 2.21 (t, 8 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CO}$), 1.81 (m, 8 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2O}$), 1.71 (m, 8 H; $\mathrm{NHCOCH_2}\mathit{CH}_2\mathrm{CH_2}$), 1.62 (m, 8 H; $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_2N}$), 1.51 (m, 8 H; $\mathit{CH}_2\mathrm{CH_2CH_2O}$), 1.39 (br s, 4 H; $\mathrm{NCH_2}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_2N}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 173.0$ (4 C; $\mathrm{NH}\mathit{C}\mathrm{O{-}CH_2}$), 159.6 (8 C; C-4), 145.1 (4 C; C-1′), 132.5 (8 C; C-3′), 131.3 (4 C; C-1), 128.2 (8 C; C-2), 126.9 (8 C; C-2′), 119.0 (4 C; CN), 115.0 (8 C; C-3), 110.0 (8 C; C-4′), 67.8 (16 C; $\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 53.7 (2 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$), 51.8 (4 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NHCO}$), 38.1 (4 C; $\mathit{C}\mathrm{H_2NHCOCH_2}$), 36.5 (4 C; $\mathrm{NHCO}\mathit{C}\mathrm{H_2}$), 29.0, 25.8, 24.3 (12 C; $(\mathit{C}\mathrm{H_2})_3$), 27.0 (16 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NHCO}$), 24.5 (14 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$ {2C} + $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$ {12C}); IR (KBr): $\tilde{\nu} = 2992$ ($\mathrm{CH_2}$), 2224 ($\mathrm{C{\equiv}N}$), 1638 cm^{-1} ($\mathrm{C{=}O}$); FAB-MS *m/z*: 1483 $[M+\mathrm{H}]^+$; calcd $\mathrm{C_{92}H_{108}N_{10}O_8}$ 1481.93.

DAB-*dendr*-(NHCO–C$_5$–CBPh)$_{16}$ (**5**): A solution of DAB-*dendr*-$(\mathrm{NH_2})_{16}$ (203.0 mg, 0.120 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) was added slowly to a solution of activated ester **2** (1.00 g, 2.10 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL). After stirring for 4 days, the solution was diluted with $\mathrm{CH_2Cl_2}$ and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted with $\mathrm{CH_2Cl_2}$. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in $\mathrm{CH_2Cl_2}$ and precipitated twice by slowly adding *n*-heptane. The precipitate was dissolved in $\mathrm{CH_2Cl_2}$, washed with demineralized water and dried over sodium sulphate yielding **5** (250 mg, 34 %) as a pale brownish solid. g 25 °C M 127 °C I; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.64$ (d, $J = 8.6$ Hz, 32 H; H-3), 7.57 (d, $J = 8.6$ Hz, 32 H; H-2), 7.46 (d, $J = 8.9$ Hz, 32 H; H-2′), 7.12 (t, 16 H; $\mathrm{CH_2N}\mathit{H}\mathrm{CO}$), 6.91 (d, $J = 8.8$ Hz, 32 H; H-3′), 3.94 (t, 32 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 3.27 (br d, 32 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{NHCO}$), 2.36 (br s, 84 H; $\mathrm{N}\mathit{CH}_2\mathrm{CH_2}\mathit{CH}_2\mathrm{N}$ and $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_2}\mathit{CH}_2\mathrm{N}$), 2.24 (t, 32 H; $\mathrm{NHCO}\mathit{CH}_2\mathrm{CH_2}$), 1.79 (m, 32 H; $\mathit{CH}_2\mathrm{CH_2O}$), 1.71 (m, 32 H; $\mathrm{NHCOCH_2}\mathit{CH}_2$), 1.60 (m, 56 H; $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_2N}$), 1.50 (m, 32 H; $\mathit{CH}_2\mathrm{CH_2CH_2O}$), 1.45 (br s, 4 H; $\mathrm{NCH_2}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_2N}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 173.4$ (16 C; $\mathrm{NH}\mathit{C}\mathrm{O{-}CH_2}$), 159.6 (32 C; C-4′), 144.5 (16 C; C-1), 132.5 (32 C; C-3), 130.3 (16 C; C-1′), 128.2 (32 C; C-2′), 126.9 (32 C; C-2), 119.0 (16 C; CN), 115.0 (32 C; C-3′), 110.0 (32 C; C-4), 67.8 (16 C; $\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 54.5 (2 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$), 52.1 (br, 24 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N}$), 51.3 (16 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NHCO}$), 37.8 (16 C; $\mathit{C}\mathrm{H_2NHCOCH_2}$), 36.3 (16 C; $\mathrm{NHCO}\mathit{C}\mathrm{H_2}$), 29.0, 25.8, 24.3 (48 C; $(\mathit{C}\mathrm{H_2})_3$), 27.0 (16 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NHCO}$), 24.5 (14 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$ {2 C} + $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$ {12 C}); IR (KBr): $\tilde{\nu} = 2992$ ($\mathrm{CH_2}$), 2225 ($\mathrm{C{\equiv}N}$), 1639 cm^{-1} ($\mathrm{C{=}O}$); MALDI-TOF-MS: *m/z*: 6348.4 $[M+\mathrm{H}]^+$; calcd $\mathrm{C_{472}H_{640}N_{46}O_{32}}$ 6346.7.

DAB-*dendr*-(NHCO–C$_5$–CBPh)$_{64}$ (**6**): A solution of DAB-*dendr*-$(\mathrm{NH_2})_{64}$ (220.1 mg, 0.031 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) was added slowly to a solution of activated ester **2** (1.00 g, 2.10 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL). After stirring for 4 days, the solution was diluted with $\mathrm{CH_2Cl_2}$ and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted with $\mathrm{CH_2Cl_2}$. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in $\mathrm{CH_2Cl_2}$ and precipitated twice by addition of MeOH and *n*-hexane. The precipitate was dissolved in $\mathrm{CH_2Cl_2}$, washed with demineralized water and dried over sodium sulphate yielding of pure **6** (240 mg, 33 %) as a pale brownish solid. g 13 °C M 132 °C I; ^{1}H NMR ($\mathrm{CDCl_3/CD_3OD}$, 95:5, 333 K): $\delta = 7.59$ (d, $J = 8.0$ Hz, 128 H; H-3′), 7.53 (d, $J = 8.0$ Hz, 128 H; H-2′), 7.42 (d, $J = 8.4$ Hz, 128 H; H-2), 6.87 (d, $J = 8.5$, 128 H; H-3), 3.91 (t, 128 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{O}$), 3.20 (br d, 128 H; $\mathrm{CH_2}\mathit{CH}_2\mathrm{NHCO}$), 2.39 (br d, 372 H; $\mathrm{N}\mathit{CH}_2\mathrm{CH_2}\mathit{CH}_2\mathrm{N}$ and $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_2}\mathit{CH}_2\mathrm{N}$), 2.21 (t, 128 H; $\mathrm{NHCO}\mathit{CH}_2\mathrm{CH_2}$), 1.76 (m, 128 H; $\mathit{CH}_2\mathrm{CH_2O}$), 1.68 (m, 128 H; $\mathrm{NHCOCH_2}\mathit{CH}_2$), 1.61 (m, 248 H; $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_2N}$), 1.49 (m, 128 H; $\mathit{CH}_2\mathrm{CH_2CH_2O}$); ^{13}C NMR ($\mathrm{CDCl_3/CD_3OD}$, 95:5, 333 K): $\delta = 173.9$ (64 C; $\mathrm{NH}\mathit{C}\mathrm{O{-}CH_2}$), 159.5 (28 C; C-4), 145.0 (64 C; C-1′), 132.4 128 C; C-3′), 131.1(64 C; C-1), 128.4(128 C; C-2), 126.9 (128 C; C-2′), 118.9 (64 C; CN), 114.8 (128 C; C-3), 109.7 (128 C; C-4′), 67.7 (64 C; $\mathrm{O}\mathit{C}\mathrm{H_2CH_2}$), 51.7 (br, 112 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N}$), 51.0 (64 C; $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NHCO}$), 37.5 (64 C; $\mathit{C}\mathrm{H_2NHCOCH_2}$), 36.0 (64 C; $\mathrm{CH_2NHCO}\mathit{C}\mathrm{H_2}$), 28.8, 25.6, 26.0 (192 C; $(\mathit{C}\mathrm{H_2})_3$), 27.1 (64 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NHCO}$), 24.5 (62 C; $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$ {2 C} + $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$ {60 C}; IR (KBr): $\tilde{\nu} = 2986$ ($\mathrm{CH_2}$), 2225 ($\mathrm{C{\equiv}N}$), 1640 cm^{-1} ($\mathrm{C{=}O}$).

11-[(4′-Cyano(1,1′-biphenyl)-4-yl)oxy]undecanoic acid (7): A mixture of 18-crown-6 (0.34 g, 1.3 mmol), finely ground potassium carbonate (4.6 g, 33 mmol), 4′-cyano-4-hydroxybipenyl (3.0 g, 15.4 mmol), and methyl-11-bromoundecanoate (5.9 g, 21.1 mmol) in acetone (40 mL) was stirred vigorously and heated under reflux overnight. The mixture was filtered, concentrated in vacuo, and recrystallized from EtOH yielding **7** as a white solid (4.67 g, 80 %). M.p. 103.5 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 8.6$ Hz, 2H; H-3′), 7.64 (d, $J = 8.6$ Hz, 2H; H-2′), 7.53 (d, $J = 8.8$ Hz, 2H; H-2), 6.99 (d, $J = 8.8$ Hz, 2H; H-3), 4.01 (t, 2H; $CH_2C\mathit{H}_2O$), 3.67 (s, 3H; $COOC\mathit{H}_3$), 2.31 (t, 2H; $CH_2C\mathit{H}_2COO$), 1.81 (m, 2H; $C\mathit{H}_2CH_2O$), 1.63 (m, 2H; $C\mathit{H}_2CH_2COO$), 1.47 (m, 2H; $C\mathit{H}_2CH_2CH_2O$), 1.34 (brs, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 174.3$ ($CH_2\mathit{C}OO$), 159.8 (C-4), 145.3 (C-1′), 132.5 (C-3′), 131.3 (C-1), 128.3 (C-2), 127.1 (C-2′), 119.1 ($\mathit{C}N$), 115.1 (C-3), 110.0 (C-4′), 68.2 ($O\mathit{C}H_2CH_2$), 51.4 ($COO\mathit{C}H_3$), 34.1 ($\mathit{C}H_2COO$), 29.5–29.1, 26.0, 24.9 ($(\mathit{C}H_2)_8$); IR (KBr): $\tilde{\nu} = 2927$ (CH_2), 2223 ($C\equiv N$), 1730 cm^{-1} ($C{=}O$). This ester (3.47 g, 8.8 mmol) was added to a sodium hydroxide solution (50 mL, 3 M). THF (ca. 50 mL) was then added until a homogeneous suspension was formed. This suspension was stirred at room temperature for 3 days, during which the reaction was monitored with TLC. On complete hydrolysis, the mixture was neutralized with a solution of hydrochloric acid (ca. 5 M) at 0 °C. The crude product was obtained as a white precipitate, which was filtered off and washed with diethyl ether and water. The crude product was recrystallized from EtOH to yield pure acid **7** (2.56 g, 76 %) as a white solid. M.p. 173.7 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 6.5$ Hz, 2H; H-3′), 7.63 (d, $J = 6.5$ Hz, 2H; H-2′), 7.52 (d, $J = 8.7$ Hz, 2H; H-2), 7.99 (d, $J = 8.7$ Hz, 2H; H-3), 4.00 (t, 2H; $CH_2C\mathit{H}_2O$), 2.35 (t, 2H; $CH_2C\mathit{H}_2COO$), 1.82 (m, 2H; $C\mathit{H}_2CH_2O$), 1.63 (m, 2H; $C\mathit{H}_2CH_2COO$), 1.47 (m, 2H; $C\mathit{H}_2CH_2CH_2O$), 1.31 (brs, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 179.9$ ($CH_2\mathit{C}OO$), 159.8 (C-4), 145.3 (C-1′), 132.5 (C-3′), 131.2 (C-1), 128.3 (C-2), 127.0 (C-2′), 119.1 ($\mathit{C}N$), 115.1 (C-3), 110.0 (C-4′), 68.1 ($O\mathit{C}H_2CH_2$), 33.9 ($\mathit{C}H_2COO$), 29.5–29.0, 26.0, 24.7 ($(\mathit{C}H_2)_8$); IR (KBr): $\tilde{\nu} = 3462$ (O–H), 2921 (CH_2), 2224 ($C\equiv N$), 1703 cm^{-1} ($C{=}O$); $C_{24}H_{29}NO_3$ (379.50): calcd C 75.96, H 7.70, N 3.69; found C 75.9, H 7.7, N 3.7.

Pentafluorophenyl-11-[(4′-cyano(1,1′-biphenyl)-4-yl)oxy]undecanoate (8): A solution of acid **7** (3.8 g, 10 mmol) and pentafluorophenol (2.05 g, 11.1 mmol) was prepared in dry DMF (100 mL). The homogeneous solution was cooled at 0 °C, and DCC (2.10 g, 10.2 mmol) in DMF (2 mL) was added in portions. After complete addition of DCC, the temperature of the reaction mixture was allowed to equilibrate to room temperature. After 3 days the reaction mixture was filtered, and the filtrate concentrated in vacuo. The crude product was recrystallized from EtOH to yield crude **8** (4.4 g, 81 %) (purity >95 % from ^{1}H NMR). Additional column chromatography (SiO_2: *n*-hexane/$CHCl_3$, 35:65, $R_f = 0.36$) yielded pure **8** (3.69 g, 62 %) as a white solid. ^{1}H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 4.7$ Hz, 2H; H-3′), 7.64 (d, $J = 4.7$ Hz, 2H; H-2′), 7.52 (d, $J = 6.8$ Hz, 2H; H-2), 6.99 (d, $J = 6.8$ Hz, 2H; H-3), 4.01 (t, 2H; $CH_2C\mathit{H}_2O$), 2.66 (t, 2H; $CH_2C\mathit{H}_2COO$), 1.78 (m, 4H; $C\mathit{H}_2CH_2O$), 1.39 (m, 12H); ^{13}C NMR ($CDCl_3$): $\delta = 169.8$ ($CH_2\mathit{C}OO$), 159.8 (C-4), 145.3 (C-1′), 132.5 (C-3′), 131.2 (C-1), 128.3 (C-2), 127.0 (C-2′), 119.1 ($\mathit{C}N$), 115.0 (C-3), 110.0 (C-4′), 68.1 ($O\mathit{C}H_2CH_2$), 33.3 ($\mathit{C}H_2COO$), 29.4–28.2, 26.0, 24.7 ($(\mathit{C}H_2)_8$); IR (KBr): $\tilde{\nu} = 2932$ (CH_2), 2229 ($C\equiv N$), 1785 cm^{-1} ($C{=}O$); $C_{30}H_{28}F_5NO_3$ (545.55): calcd C 66.05, H 5.17, N 2.56; found C 66.4, H 5.3, N 2.5.

Propyl-NHCO–C$_{10}$–CBPh (9): *n*-Propylamine (0.2 g, 3.4 mmol) was slowly added to a solution of activated ester **8** (1.00 g, 1.83 mmol) in CH_2Cl_2 (40 mL). After stirring for 5 days, the solution was diluted with CH_2Cl_2 and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted with CH_2Cl_2. The combined organic phases consequently were washed with demineralized water, dried with sodium sulphate, and concentrated in vacuo yielding pure **9** (580 mg, 75 %) as a white solid. K 105 °C I; ^{1}H NMR ($CDCl_3$): $\delta = 7.67$ (d, $J = 7.9$ Hz, 2H; H-3′), 7.63 (d, $J = 8.1$ Hz, 2H; H-2′), 7.52 (d, $J = 8.9$ Hz, 2H; H-2), 6.99 (d, $J = 8.8$ Hz, 2H; H-3), 5.43 (brs, 1H; $CH_2N\mathit{H}CO$), 4.00 (t, 2H; $CH_2C\mathit{H}_2O$), 3.22 (q, 2H; $CH_2C\mathit{H}_2NH$), 2.26 (t, 2H; $CH_2C\mathit{H}_2CON$), 1.80 (m, 2H; $C\mathit{H}_2CH_2O$), 1.7–1.3 (brm, 14H), 0.92 (t, 3H; $NHCH_2CH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$): $\delta = 173.9$ ($CH_2\mathit{C}ONH$), 159.8 (C-4), 148.8 (C-1′), 145.3 (C-3′), 132.5 (C-1), 131.2 (C-2), 128.3 (C-2′), 127.0 ($\mathit{C}N$), 115.1 (C-3), 110.0 (C-4′), 68.14 ($O\mathit{C}H_2CH_2$), 41.1 ($\mathit{C}H_2NH$), 36.9 ($\mathit{C}H_2COO$), 29.5–29.0, 25.8 ($(\mathit{C}H_2)_8$), 22.9 ($CH_3\mathit{C}H_2CH_2NHCO$), 11.3 ($\mathit{C}H_3CH_2CH_2NHCO$); IR (KBr): $\tilde{\nu} = 2990$ (CH_2), 2236 ($C\equiv N$), 1637 cm^{-1} ($C{=}O$); FAB-MS *m/z*: 421 $[M+H]^+$; calcd $C_{27}H_{35}N_2O_2$ 419.59.

DAB-*dendr*-(NHCO–C$_{10}$–CBPh)$_4$ (10): A solution of DAB-*dendr*-$(NH_2)_4$ (136.7 mg, 0.432 mmol) in CH_2Cl_2 (2 mL) was added slowly to a solution of activated ester **8** (0.99 g, 1.81 mmol) in CH_2Cl_2 (40 mL). After stirring for 5 days, the solution was diluted with CH_2Cl_2 and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted with CH_2Cl_2. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in CH_2Cl_2 and precipitated twice by slowly adding *n*-hexane, yielding pure **10** (520 mg, 68 %) as a tan solid. K 106 °C M 114 °C I; ^{1}H NMR ($CDCl_3$): $\delta = 7.68$ (d, $J = 7.9$ Hz, 8H; H-3), 7.63 (d, $J = 8.2$ Hz, 8H; H-2), 7.51 (d, $J = 8.8$ Hz, 8H; H-2′), 6.98 (d, $J = 8.8$ Hz, 8H; H-3′), 6.49 (t, 4H; $CH_2N\mathit{H}COCH_2$), 3.99 (t, 8H; $CH_2C\mathit{H}_2O$), 3.29 (q, 8H; $CH_2C\mathit{H}_2NH$), 2.42 (t, 8H; $NC\mathit{H}_2CH_2CH_2NH$), 2.36 (brs, 4H; $NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N$), 2.16 (t, 8H; $CH_2C\mathit{H}_2CO$), 1.79 (m, 8H; $CH_2C\mathit{H}_2CH_2O$), 1.62 (m, 8H; $NHCOCH_2C\mathit{H}_2CH_2$), 1.5–1.2 (brm, 76H); ^{13}C NMR ($CDCl_3$): $\delta = 173.4$ (4C; $NH\mathit{C}O{-}CH_2$), 159.7 (8C; C-4′), 145.2 (4C; C-1), 132.5 (8C; C-3), 131.1 (4C; C-1′), 128.2 (8C; C-2′), 127.0 (8C; C-2), 119.0 (4C; $\mathit{C}N$), 115.0 (8C; C-3′), 110.0 (8C; C-4), 68.0 (16C; $O\mathit{C}H_2CH_2$), 53.6 (2C; $N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N$), 51.7 (4C; $N\mathit{C}H_2CH_2CH_2NHCO$), 38.0 (4C; $\mathit{C}H_2NHCOCH_2$), 36.7 (4C; $NHCO\mathit{C}H_2$), 29.5–29.2, 26.0, 25.9 (32C; $(\mathit{C}H_2)_8$), 26.9 (4C; $NCH_2\mathit{C}H_2CH_2NHCO$), 24.7 (2C; $NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N$); IR (KBr): $\tilde{\nu} = 2990$ (CH_2), 2225 ($C\equiv N$), 1639 cm^{-1} ($C{=}O$); FAB-MS *m/z*: 1764 $[M+H]^+$; calcd $C_{112}H_{148}N_{10}O_8$ 1762.46.

DAB-*dendr*-(NHCO–C$_{10}$–CBPh)$_{16}$ (11): A solution of DAB-*dendr*-$(NH_2)_{16}$ (188.1 mg, 0.112 mmol) in CH_2Cl_2 (2 mL) was added slowly to a solution of activated ester **8** (0.98 g, 1.80 mmol) in CH_2Cl_2 (40 mL). After stirring for 5 days, the solution was diluted with CH_2Cl_2 and MeOH, and extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted with CH_2Cl_2. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in CH_2Cl_2 and precipitated twice by slowly adding *n*-hexane, yielding pure **11** (420 mg, 50 %) as a tan solid. K 105 °C M 124 °C I; ^{1}H NMR ($CDCl_3$): $\delta = 7.65$ (d, $J = 8.3$ Hz, 32H; H-3′), 7.60 (d, $J = 8.3$ Hz, 32H; H-2′), 7.50 (d, $J = 8.7$ Hz, 32H; H-2), 6.96 (brt, 16H; $CH_2N\mathit{H}COCH_2$), 6.95 (d, $J = 8.7$ Hz, 32H; H-3), 3.96 (t, 32H; $CH_2C\mathit{H}_2O$), 3.26 (brd, 32H; $CH_2C\mathit{H}_2NH$), 2.38 (brs, 84H; $NC\mathit{H}_2CH_2C\mathit{H}_2N$ and $NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N$), 2.24 (t, 32H; $CH_2C\mathit{H}_2CO$), 1.77 (m, 32H; $C\mathit{H}_2CH_2O$), 1.5–1.2 (brm, 280H); ^{13}C NMR ($CDCl_3$): $\delta = 173.7$ (16C; $NH\mathit{C}O{-}CH_2$), 159.7 (32C; C-4), 145.1 (16C; C-1′), 132.5 (32C; C-3′), 131.2 (16C; C-1), 128.3 (32C; C-2), 127.0 (32C; C-2′), 119.0 (16C; $\mathit{C}N$), 115.0 (32C; C-3), 110.0 (32C; C-4′), 68.1 (16C; $O\mathit{C}H_2CH_2$), 54.5 (2C; $N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N$), 52.1 (br, 24C; $N\mathit{C}H_2CH_2\mathit{C}H_2N$), 51.3 (16C; $N\mathit{C}H_2CH_2CH_2NHCO$), 37.7 (16C; $\mathit{C}H_2NHCOCH_2$), 36.6 (16C; $CH_2NHCO\mathit{C}H_2$), 29.6–29.4, 29.0, 25.9, 25.8 (128C; $(\mathit{C}H_2)_8$), 27.0 (16C; $NCH_2\mathit{C}H_2CH_2NHCO$), 24.5 (14C; $NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N$ {2C} + $NCH_2\mathit{C}H_2CH_2N$ {12C}); IR (KBr): $\tilde{\nu} = 2982$ (CH_2), 2225 ($C\equiv N$), 1639 cm^{-1} ($C{=}O$); MALDI-TOF-MS: *m/z*: 7449 $[M+H]^+$, 7471 $[M+Na]^+$, 7487 $[M+K]^+$; calcd $C_{472}H_{640}N_{46}O_{32}$ 7470.54.

DAB-*dendr*-(NHCO–C$_{10}$–CBPh)$_{64}$ (12): A solution of DAB-*dendr*-$(NH_2)_{64}$ (214.1 mg, 0.0300 mmol) in CH_2Cl_2 (2 mL) was added slowly to a solution of activated ester **8** (0.99 g, 1.81 mmol) in CH_2Cl_2 (40 mL). After stirring for 5 days, the solution was extracted with a saturated sodium carbonate solution, and the aqueous phase was further extracted three times with CH_2Cl_2. The combined organic phases were dried with sodium sulphate and concentrated in vacuo. The crude product was taken up in a mixture of CH_2Cl_2/MeOH (95:5) and precipitated three times by slowly adding *n*-hexane, yielding **12** (340 mg, 40 %) as a tan solid. K 103 °C M 135 °C I; ^{1}H NMR ($CDCl_3$, 333 K): $\delta = 7.59$ (d, $J = 8.4$ Hz, 128H; H-3′), 7.55 (d, $J = 8.2$ Hz, 128H; H-2′), 7.44 (d, $J = 8.7$ Hz, 128H; H-2), 6.90 (d, $J = 8.7$, 128H; H-3), 3.93 (t, 128H; $CH_2C\mathit{H}_2O$), 3.23 (brd, 128H; $CH_2C\mathit{H}_2NHCO$), 2.38 (brd, 372H; $NC\mathit{H}_2CH_2C\mathit{H}_2N$ and $NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N$), 2.17 (t, 128H; $NHCOC\mathit{H}_2CH_2$), 1.73 (m, 128H; $C\mathit{H}_2CH_2O$), 1.60 (m, 128H; $NHCOCH_2C\mathit{H}_2$), 1.41 (m, 248H; $NCH_2C\mathit{H}_2CH_2N$), 1.49 (brm, 1024H); ^{13}C NMR ($CDCl_3$): $\delta = 174.0$ (64C; $NH\mathit{C}O{-}CH_2$), 159.7 (128C; C-4), 145.0 (64C; C-1′), 132.5 (128C; C-3′), 131.2 (64C; C-1), 128.3 (128C; C-2), 127.0 (128C; C-2′), 119.0 (64C; $\mathit{C}N$), 115.0 (128C; C-3), 110.0 (128C; C-4′), 68.0 (64C; $O\mathit{C}H_2CH_2$), 52.0 (br, 112C; $N\mathit{C}H_2CH_2\mathit{C}H_2N$), 51.1 (64C; $N\mathit{C}H_2CH_2CH_2NHCO$), 37.5 (64C; $\mathit{C}H_2NHCOCH_2$), 36.6 (64C; $CH_2NHCO\mathit{C}H_2$), 29.7–29.5, 29.2, 26.1, 26.0 (512C; $(\mathit{C}H_2)_8$), 27.1 (64C; $NCH_2\mathit{C}H_2CH_2NHCO$), 24.5 (62C; $NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N$ {2C} + $NCH_2\mathit{C}H_2CH_2N$ {60C}); IR (KBr): $\tilde{\nu} = 2986$ (CH_2), 2226 ($C\equiv N$), 1639 cm^{-1} ($C{=}O$).

Acknowledgments: This research was supported by the Netherlands Foundation for Chemical research (SON) and by the Netherlands Organization for Scientific research (NWO). DSM Research (Manon Muré-Mak) is gratefully acknowledged for an unrestricted research grant and for providing us with samples of the poly(propylene imine) dendrimers. The authors would like to thank J. B. Cristensen for performing FAB-MS measurements, L. Groenendaal for performing MALDI-TOF-MS measurements, H. Eding for Elemental Analyses and Prof. D. Broer (Philips Research, TUE) and Marcel van Genderen (TUE) for stimulating discussions.

Received: April 14, 1998 [F1091]

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