Extended-Core Discotic Liquid Crystals Based on the Intramolecular H-Bonding in *N*-Acylated 2,2′-Bipyridine-3,3′-diamine Moieties

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Abstract: A new type of disc-shaped molecule (**1a–c**) has been synthesised and characterised. The molecules were built up by linking three lipophilic, *N*-monoacylated 2,2′-bipyridine-3,3′-diamine wedges to a central 1,3,5-benzenetricarbonyl unit. They show liquid crystalline behaviour, as shown by DSC, polarisation microscopy and X-ray diffraction. In all cases the mesophase was characterised as a D_{ho} phase. From ^{1}H NMR results it was shown that the interior of compounds **1a–c** preferentially adopts a C_3 symmetrical conformation owing to strong intramolecular H-bonding, which gives rise to an extended core. This large core induces strong interactions between molecules, leading to mesophases of enhanced thermal stability.

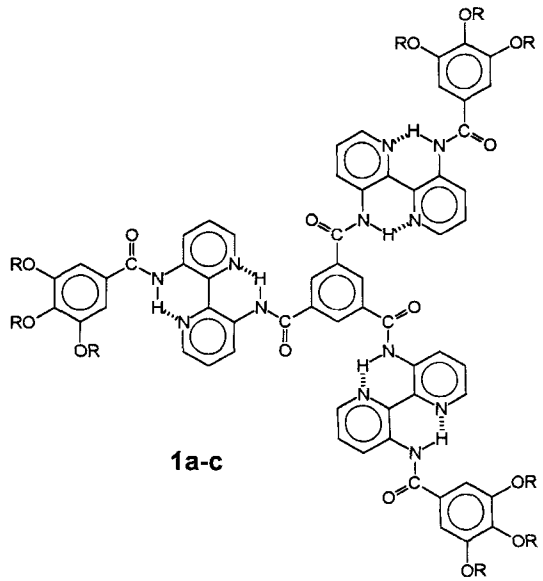
Keywords
bipyridines · discotic liquid crystals · hydrogen bonds · liquid crystals · mesophases

Introduction

Since its beginnings in 1977,[1] the field of discotic liquid crystals has expanded exponentially. A recent new development is the synthesis of discotic liquid crystals of increased dimensions,[2a–g] containing cores with diameters exceeding 20 Å. They are much larger than the commonly used and well-studied cores based on benzene or triphenylene, which have diameters of around 10 Å. One of the major consequences of the larger cores is to extend the temperature range of liquid crystallinity. Potential applications for which enhanced temperature stability of mesophases is desirable include one-dimensional charge transport.[3a–b]

Although a wide variety of central cores are currently known to induce discotic liquid crystalline behaviour, there are only limited reports of columnar mesophases based on large discs built up through *inter*molecular H-bonding between wedges.[4a–c] *Intra*molecular H-bonding has also only seldom been used to improve the rigidity of an otherwise flexible core.[5] Without a doubt, secondary interactions such as H-bonding will gain in importance as a powerful and flexible tool to control the conformation of large central cores.

We have shown recently that strong intramolecular H-bonding is present in *N*-acylated 2,2′-bipyridine-3,3′-diamines,[6] and we therefore decided to use this building block to design a new class of large disc-shaped molecules. Here, we discuss the synthesis and characterisation of compounds **1a–c** (Figure 1) in which three rigid bipyridine moieties and a central benzene ring form a large planar core. Intramolecular H-bonding and strong stacking interactions between the large molecules **1a–c** lead to enhanced stability of the mesophases.



1a-c

Figure 1. Disc-shaped compounds based on *N*-acylated 2,2′-bipyridine-3,3′-diamine (R = n-C_6H_{13} (**a**), n-$C_{12}H_{25}$ (**b**), n-$C_{18}H_{37}$ (**c**)).

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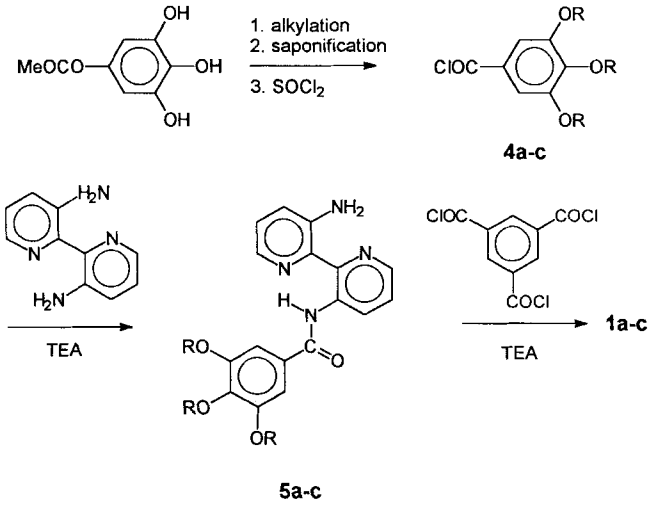
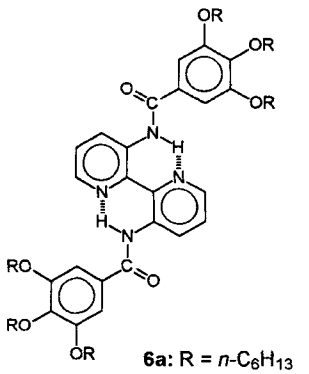
Results and Discussion

1. Synthesis: Disc-shaped molecules **1a–c** were synthesised by a convergent approach[7] (Scheme 1). The synthesis of 2,2′-bipyridine-3,3′-diamine has been described previously.[8] The hydrophobic groups in **4a–c** were introduced by alkylation of

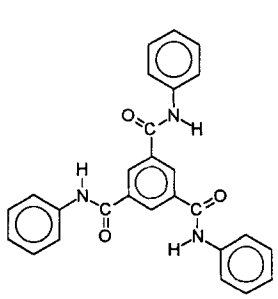


Scheme 1. Synthesis of disc-shaped compounds **1a–c** (R = n-C_6H_{13} (**a**), n-$C_{12}H_{25}$ (**b**), n-$C_{18}H_{37}$ (**c**)).

the commercially available methyl 3,4,5-trihydroxybenzoate by modifying previously described procedures.[9a–b] To obtain a high degree of monoacylation in the condensation of 2,2′-bipyridine-3,3′-diamine with acid chlorides **4a–c**, all reactions were carried out by adding a dilute solution of the acid chlorides (≈0.1 mM) to an ice-cooled and dilute solution (≈0.1 mM) of 2,2′-bipyridine-3,3′-diamine and triethylamine (TEA). Typical product ratios of mono- to diacylated compounds were 86:14, regardless of the acid chloride used. Column chromatography proved to be a useful technique to separate the monoacylated compounds **5a,b** from the diacylated compounds **6a,b**.[10] In the case of compound **5c**, solubility problems and almost identical R_f values for the mono- and diacylated products prevented complete separation by column chromatography. Compound **5c** could, however, be obtained at a purity of up to 95% and was used as such. In the final step—linking **5a–c** to benzene-1,3,5-tricarbonyl trichloride—we found that it is crucial to use a slight excess of **5a–c** to ensure complete reaction. Although acid chlorides are reactive, long reaction times, or in the case of compound **5c** even elevated temperatures, are required. The crude compounds were thoroughly purified and finally precipitated from a $CHCl_3$ solution with acetone, giving the desired compounds **1a–c** in reasonable to good yields (54–82%). Compounds **1a,b** were obtained as waxy, strongly birefringent substances at room temperature; this indicates the presence of a mesophase (vide infra). Compound **1c** was obtained as a white powder.



Compounds **7** and **8** were synthesised as references for additional studies. Reference compound **7** was obtained by condensation of aniline with benzene-1,3,5-tricarbonyl trichloride in a yield of 72%. Compound **8** was obtained in a three-step procedure. In the first step, 2,2′-bipyridine-3,3′-diamine was monoacylated with Boc_2O by heating the two compounds in THF under reflux. Similar product ratios of mono- and diacylated products were observed as in the case of the previously discussed acid chlorides. The monoacylated compound **10** was obtained in 70% yield after column chromatography. In the second step, compound **10** reacted with benzene-1,3,5-tricarbonyl trichloride—in a similar procedure as discussed for compounds **1a–c**—to give the tri-Boc derivative **9**. Finally, compound **9** was treated with trifluoroacetic acid in CH_2Cl_2 to remove the Boc group, yielding the desired triamine **8**. Reference compounds **7** and **8** were barely soluble in common organic solvents.



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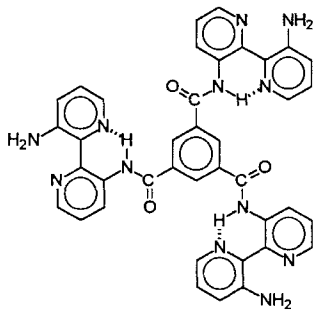

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All new compounds were fully characterised by NMR and IR spectroscopy and gave satisfactory elemental analyses. Gel permeation chromatography (GPC) measurements confirmed the high purity (>99.6%) of compounds **1a–c** with respect to higher and lower molecular weight substances. All spectroscopic data of compounds **1a–c** are in agreement with the proposed C_3-symmetric structure (Figure 1) and will be presented in Section 2. The properties of these new molecules were studied in detail by means of differential scanning calorimetry (DSC), polarisation microscopy and X-ray diffraction, and the results will be given in Sections 3–5.

2. ^{1}H NMR spectroscopy: It has been shown previously that strong intramolecular H-bonds in *N*-acylated 2,2′-bipyridine-3,3′-diamines lead to the formation of a planar, transoid bipyridine system.[6] In ^{1}H NMR spectra this conformation is characterised by a low-field absorption of the amide NH (at $\delta \approx 14$) and of the H-4 proton of the pyridine ring (at $\delta \approx 9.2$), which is a consequence of the deshielding influence of the adjacent carbonyl group.

The ^{1}H NMR spectra of compounds **1a–c** were recorded in $CDCl_3$ and follow the pattern described above. For example, in compound **1b** (Figure 2), two low-field NH shifts ($\delta = 15.49$ and 14.36) are present. Furthermore, the absorptions of pyridine protons H-4 and H-4′ are found at $\delta = 9.56$ and 9.38,

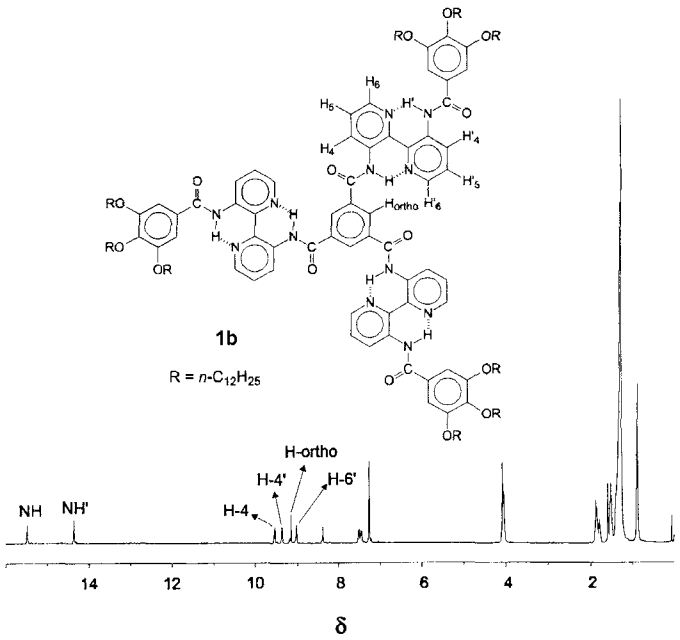

Figure 2. ^{1}H NMR spectrum of compound **1b** in $CDCl_3$

respectively. These values are in agreement with those commonly observed in acylated 2,2′-bipyridine-3,3′-diamines. However, $\delta = 9.16$ for the *ortho* hydrogens of the central benzene ring is remarkably high. Similarly high values for *ortho*-H are found in **1a** and **1c** ($\delta = 9.25$ and 9.22, respectively).

To account for this, reference compounds **7** and **8** were designed to determine the influence of the bipyridine moiety on the δ value of *ortho*-H of the central benzene ring. Both compounds are insoluble in $CDCl_3$, and $[D_7]$DMF was used for their ^{1}H NMR spectra; these are compared in Figure 3. A large difference between the absorptions of the amide NH in compound **8** ($\delta = 15.79$) and compound **7** ($\delta = 10.56$) was found, and a low-field absorption at $\delta = 9.46$ for H-4 was observed in compound **8**. Furthermore, a substantial difference in the absorptions of *ortho*-H atoms of the central benzene rings was observed for compounds **7** ($\delta = 8.81$) and **8** ($\delta = 9.23$), which cannot be attributed to electronic effects alone. A reasonable explanation is that the rotational freedom around the Ph–C=O in **7** is more pronounced than in **8**. In compound **8**, a high degree of coplanarity of the bipyridine units with the central benzene ring would induce a relative deshielding of the identical protons in the trimesoyl core. If the rotational freedom around the Ph–C=O bond is restricted in **8**, then this will certainly also be the case in compounds **1a–c**. This phenomenon is illustrated in a CPK model of compound **1b** in Figure 4, from which it is also obvious that the high degree of coplanarity of the central benzene ring with the bipyridine units implies a C_3 symmetry, for reasons of space availability.

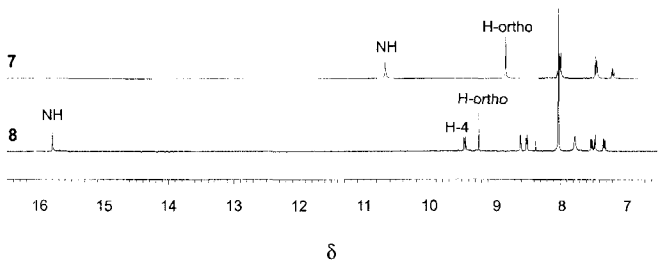

Figure 3. ^{1}H NMR spectra in $[D_7]$DMF of compounds **7** and **8**

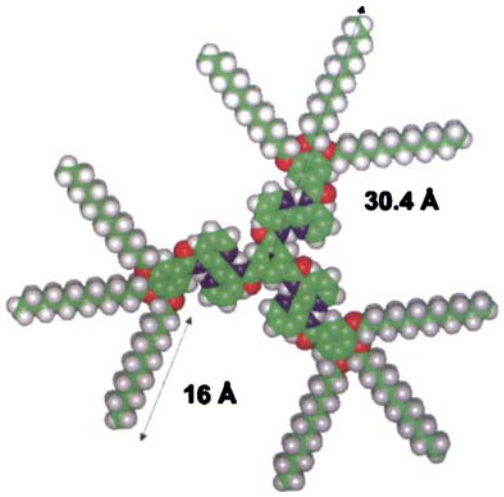

Figure 4. CPK model of compound **1b**.

The concentration effect in the ^{1}H NMR spectra of compound **1a** in $CDCl_3$ should be noted.[11] On going from higher (31 mmol L^{-1}) to lower concentrations (1.55 mmol L^{-1}) the peaks sharpened substantially and all aromatic peaks underwent some deshielding. The effect was most pronounced for the *ortho*-H of the central benzene ring and the protons in the interior of the molecule, namely, NHCO, H-4 and H-6′. A similar effect was observed when a 2.8 mM solution of **1a** in $[D_8]$toluene was heated from room temperature to 100 °C. At room temperature, the peaks were extremely broad, but sharpened at 80 °C with a concomitant deshielding of the aromatic protons. Finally, we found that, when very apolar solvents were used (hexane and cyclohexane), compounds **1a–c** did not really dissolve, but formed stable gels.[12]

All ^{1}H NMR spectroscopic results given above are in agreement with the stacking of discs in solution. In the absence of solvent this preference for phase separation leads to liquid crystalline behaviour. The preferred planar orientation of the aromatic interior leads to a large rigid core with an estimated diameter of approximately 28 Å (Figure 4) in compounds **1a–c**.

3. Differential scanning calorimetry: The phase transition temperatures and enthalpies of compounds **1a–c** and **6a,b** were determined by using DSC. The heating and cooling rates were 10 K min^{-1}. All samples were dried in a vacuum oven before use. The data are collected in Table 1. Due to the high clearing temperatures of compounds **1a–c** and the presence of air in the sealed pans, slight decomposition took place in all samples starting at 250 °C.

Compound **1a** was heated in a first run from −40 °C to 200 °C and subsequently cooled to −80 °C. No K–D_{ho} transition could be observed. In a second run the sample was heated to 400 °C, and a D_{ho}–I transition was visible at 383 °C. Due to

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Table 1. Transition temperatures (°C) and corresponding enthalpies (kJ mol^{-1}) for the phases [a] of compounds **1a–c** and compounds **6a,b** (●: phase observed; –: phase not observed).

	K	T (ΔH)	M	D_{ho}	T (ΔH)	I
1a	– [c]		–	●	383 (17) [b]	●
1b	●	9 (56)	–	●	355 (27) [b]	●
1c	●	62 (172)	–	●	308 (30) [b]	●
6a	●	53 (38)	●	–	108 (2.5)	●
6b	●	38 (79.5)	●	–	110 (2.5)	●

[a] K = crystalline phase; M = unidentified mesophase; D_{ho} = hexagonal ordered columnar phase; I = isotropic phase. [b] Clearing is accompanied by some decomposition of the sample making the accuracy of the calculated enthalpies ±2 kJ mol^{-1}. [c] On cooling to −80 °C the sample did not show a transition.

decomposition of the sample, the cooling run was rather unreliable, although a I–D_{ho} transition was present at 340 °C.

In a first run, compound **1b** was heated and cooled between −20 and 200 °C. A K–D_{ho} transition was observed at 9 °C on heating, and a D_{ho}–K transition at −3 °C on cooling. A second heating and cooling cycle between −20 and 200 °C gave the same results. In a last run the sample was heated from 20 to 380 °C and showed a D_{ho}–I transition at 355 °C, and an I–D_{ho} transition at 333 °C upon cooling.

Compound **1c** was heated and cooled in a first run between −20 and 200 °C, and a K–D_{ho} transition was observed at 62 °C and a D_{ho}–K transition at 54 °C, which was immediately followed by a second transition at 47 °C. A second heating and cooling run gave the same results. In the third run the sample was heated up to 330 °C, and a D_{ho}–I transition was observed at 308 °C. The cooling run showed an I–D_{ho} transition at 302 °C.

Comparison of the DSC data obtained for the "monomeric" reference compounds **6a,b** and the disc-shaped analogues **1a,b** reveals the striking difference in mesophase stability. While the temperature range in which compounds **6a,b** display liquid crystallinity is limited to approximately 60 °C, the corresponding range for compounds **1a,b** is more than 350 °C.

4. Polarisation microscopy: In order to study the thermal behaviour of the compounds by polarisation microscopy, samples of compounds **1a–c** were prepared on a glass plate. A strongly birefringent texture was observed for **1a,b**, indicating that these compounds were already in a mesophase at room temperature. This was confirmed by the fact that, upon heating (to around 200 °C), the samples slowly became mobile, that is, sensitive towards pressure changes, while remaining strongly birefringent. Compounds **1a,b** exhibited a permanent mesophase starting from room temperature up to the clearing temperatures at 389 and 373 °C for **1a** and **1b**, respectively.[13] In both cases, the isotropic state had a low viscosity. Typical textures for compounds **1a,b** were grown by slowly cooling the isotropic liquid (1 K min^{-1}), and an example is presented in Figure 5 (top).

Compound **1c** was obtained as a white powder, which changed into a liquid crystalline phase at around 58 °C. The clearing temperature of 320 °C was substantially lower than in **1a,b**. The fast reappearance upon cooling of the liquid crystalline phase at 317 °C indicated a high degree of preorientation in the isotropic state. Again, typical textures could be grown by slowly cooling the isotropic liquid (Figure 5, bottom). Large

Figure 5. Top: Optical texture of **1b** at room temperature (crossed polarisers). Bottom: Optical texture of **1c** at 280 °C (crossed polarisers).

homeotropic monodomains were present in the liquid crystalline state. Upon further cooling, a gradual transition into the crystalline state was observed at around 45 °C.

5. X-Ray diffraction: The structures of the mesophases of compounds **1a–c** were examined in detail by X-ray diffraction. Compound **1c** was heated in a glass capillary to the clearing point and was then slowly cooled to the liquid crystalline state at a rate of 5 K min^{-1}. At 120 °C the sample was screened to find suitably large monodomains. The diffraction pattern obtained for **1c** points unambiguously to a columnar packing of the molecules. Furthermore, two monodomains could be distinguished: a more prevalent one with the columns parallel to the X-rays and a less pronounced one with the columns perpendicular to the X-rays. The reflections in the wide-angle area originated from the second monodomain. The calculated diffraction spacings are summarised in Table 2. A sharply defined reflection at 3.5 Å and a broad ring at 4.7 Å can be assigned to the disc–disc distance and the disorder of the aliphatic chains, respectively. In the small-angle area (Figure 6) two clear reflections at 40.0 and 23.2 Å are present in a hexagonal distribution. The reflections are assigned to the 1 0 0 and 1 1 0 reflection, respectively. Finally, two less intense reflections at 20.0 and 13.8 Å are also observed, which derive from the 2 0 0 and 2 1 0 reflections. The hexagonal distribution of the 1 0 0 and 1 1 0 reflection clearly points to a hexagonal packing of the columns in the liquid crystalline state,

Table 2. Diffraction spacings in Å obtained for compounds **1a,b** at 20 °C and for compound **1c** at 120 °C.

hkl	**1a**	**1b**	**1c**
100	25.4	34.1	40.0
110	–	..	23.2
200	–	17.4	20.0
210	..	–	13.8
–	–	3.6	–
halo	4.7	4.7	4.7
interdisc	3.3	3.4	3.5
intercolumn	30	40	46

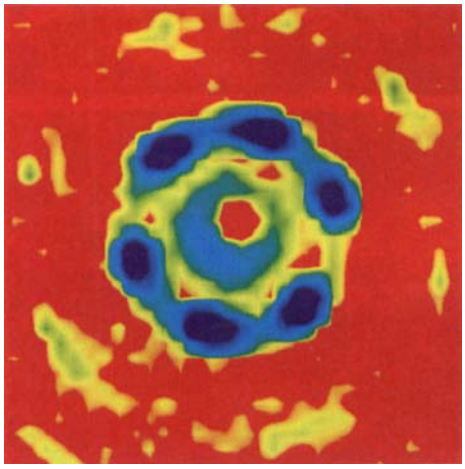

Figure 6. Diffraction pattern observed in the small-angle area for compound **1c** at 120 °C.

with an intercolumnar distance of about 46 Å. The nature of the liquid crystalline state present can thus be designated as a D_{ho} phase. Interestingly, another monodomain could be distinguished when the orientation of the glass capillary was changed. In this side-on view, a characteristic reflection with a quadruplet splitting pattern was observed.

Compounds **1a,b** were shear aligned at room temperature. Both compounds show similar diffraction patterns. The calculated diffraction spacings of compounds **1a,b** are summarised in Table 2. The diffraction patterns indicate that the molecules are packed in columns. For example in compound **1b**, two clear reflections are present in the small-angle area: a first-order reflection at 34.1 Å and a reflection split into a quadruplet at 17.4 Å. In the wide-angle area, the disorder of the aliphatic chains at 4.7 Å, a sharp reflection at 3.4 Å and a more diffuse reflection at 3.6 Å are observed. The mesophase present in compounds **1a,b** is most likely to be a D_{ho} phase, because of the similarities between the X-ray diffraction pattern obtained for **1c** in the side-on view and the those found for compounds **1a,b**. Unfortunately, we have not yet been able to explain the origin of this set of reflections. One explanation can be derived from the CPK model in Figure 4. Compounds **1a–c** are not perfectly disc-shaped; they are more accurately described as trefoil-shaped. To minimise unfavourable interactions and to fill the space between the bipyridine moieties, it is likely that a given disc will be rotated with respect to the previous and following disc. Possibly, an extra order is thus present in the lattice. Experiments with an optically active homologue are in progress and will hopefully clarify the origin of the splitting in the quadruplet reflections.

Conclusions

A new class of discotic liquid crystals based on 2,2′-bipyridine-3,3′-diamine has been synthesised in a convergent sequence, and the molecules have been fully characterised. ^{1}H NMR spectroscopy has revealed that intramolecular H-bonding forces the 3,3′-di(carbonylamino)-2,2′-bipyridine fragment of each wedge into a planar conformation. Furthermore, evidence has been presented that the core as a whole possesses a high degree of planarity in solution and has a diameter of approximately 28 Å. It has been deduced from concentration and temperature measurements that the molecules have a strong tendency to aggregate in solution, which is promoted in very apolar solvents, by higher concentrations and by lower temperatures. Compounds **1a–c** show liquid crystalline behaviour relying on several cooperative processes. Firstly, strong intramolecular hydrogen bonding in the *N*-acylated 2,2′-bipyridine-3,3′-diamine moieties fixes the bipyridine units in a planar, transoid conformation. Secondly, the central benzene-1,3,5-tricarbonyl unit preferentially adopts a planar conformation in which all carbonyl groups point in the same direction giving rise to a C_3 symmetry and to an extended planar core incorporating the bipyridine units. Thirdly, the presence of peripheral lipophilic nonaromatic side chains induces liquid crystalline behaviour, and the mesophase present in compounds **1a–c** can be designated as a D_{ho} phase.

Experimental Procedure

General: ^{1}H NMR spectra were recorded on a Bruker AM-400 (400.13 MHz). IR spectra were measured on a Perkin Elmer 1600 FT-IR. Elemental analyses were carried out using a Perkin Elmer 240. The optical properties of the materials were studied with a Jenaval polarisation microscope equipped with a Linkam THMS 600 heating device, with crossed polarisers. Melting points were recorded on an Linkam THMS 600 heating device. DSC spectra were obtained on a Perkin-Elmer DSC-7 under a nitrogen atmosphere with heating and cooling rates of 10 K min^{-1}. The transitions into the isotropic state of compounds **1a–c** were determined by means of DSC. X-ray diffraction patterns of oriented and nonoriented samples were recorded using a multiwire area detector X-1000 coupled with a graphite monochromator and a Linkam THM 600 hot stage at elevated temperatures, or by means of a flat-film camera at room temperature (Ni filtered, $Cu_{K\alpha}$ radiation). The temperature was adjustable to an accuracy of ± 0.5 K. For the GPC measurements, a column with PL gel (5 μL particles and 500 Å pore size) was used with chloroform as eluent and a flow of 1 mL min^{-1}, and a UV detector was used at a wavelength of 254 nm. Fast-atom bombardment mass spectra (FAB-MS) were recorded on a VG micromass VG 7070 E using a Xe beam at 8 kV with nitrobenzyl alcohol (NOBA) as matrix. Diethyl ether was dried over $CaCl_2$ and stored over Na wire, THF was distilled from Na/benzophenone, and CH_2Cl_2 was dried over $CaCl_2$ and distilled from P_2O_5. All other chemicals were used as received.

Methyl 3,4,5-trihexyloxybenzoate (2a): A mixture of methyl 3,4,5-trihydroxybenzoate (10 g, 54.3 mmol), 1-bromohexane (29 g, 175 mmol) and anhydrous K_2CO_3 (40 g) was stirred under an Ar atmosphere in dimethylformamide (200 mL) at 75 °C for 6 h. The reaction mixture was allowed to cool to room temperature, poured into water and extracted with hexane (2 × 250 mL). The combined organic layers were washed with HCl (1 M, 200 mL) and saturated $NaHCO_3$ solution (200 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The residual yellow oil was purified by column chromatography (SiO_2). The impurities were first eluted (eluent: hexane), followed by compound **2a** (eluent: hexane/EtOAc 85/15, $R_f = 0.50$). This afforded pure **2a** as a colourless oil (20.3 g, 85%). ^{1}H NMR ($CDCl_3$): $\delta = 7.22$ (s, 2H, *ortho*-H); 4.03 (m, 6H, OCH_2); 3.88 (s, 3H, OCH_3); 1.80 (m, 6H, OCH_2CH_2); 1.48 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 12H, $(CH_2)_2$); 0.90 (t, 9H, CH_3).

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3,4,5-Trihexyloxybenzoic acid (3a): A mixture of **2a** (10 g, 23.6 mmol) and KOH (2.7 g) in EtOH (96%, 200 mL) was heated under reflux for 4 h. Concentrated HCl (6 mL) was then added to the hot solution, followed by H_2O (200 mL). Extraction with diethyl ether (3 × 200 mL) yielded the crude product, which was purified by column chromatography (SiO_2). Impurities eluted first (eluent: CH_2Cl_2), followed by **3a** (eluent: CH_2Cl_2/CH_3CN 1/1, $R_f = 0.62$). Compound **3a** was obtained as a slowly solidifying white solid (7.35 g, 76%). M.p. 41–42.5 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.27$ (s, 2H, *ortho*-H); 4.02 (m, 6H, OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.46 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 12H, $(CH_2)_2$); 0.88 (t, 9H, CH_3). Anal. calcd. for $C_{25}H_{42}O_5$ (MW 422.60): C 71.05, H 10.01. Found: C 71.0, H 9.9.

3,4,5-Trihexyloxybenzoyl chloride (4a): Compound **3a** (4.1 g, 9.7 mmol) was treated with thionyl chloride (50 mL) under reflux for 3 h. The excess thionyl chloride was distilled off, and the resulting brown oil was flushed with hexane (2 × 10 mL). The brown oil was dissolved in hexane and filtered. After concentration of the filtrate in vacuo, **4a** was obtained as a yellow oil (3.65 g, 85%).^{1}H NMR ($CDCl_3$): $\delta = 7.30$ (s, 2H, *ortho*-H); 4.02 (t, 2H, *para*-OCH_2); 3.98 (t, 4H, *meta*-OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.48 (m, 6H, $OCH_2CH_2CH_2$); 1.28 (m, 12H, $(CH_2)_2$); 0.88 (t, 9H, CH_3).

3′-(3,4,5-Trihexyloxybenzoylamino)-2,2′-bipyridine-3-amine (5a): A solution of **4a** (3.54 g, 8 mmol) in dry diethyl ether (70 mL) was added dropwise under an Ar atmosphere to an ice-cooled solution of 2,2′-bipyridine-3,3′-diamine (1.49 g, 8 mmol) and triethylamine (TEA) (1.3 mL) in dry diethyl ether (70 mL). After complete addition, the ice bath was removed, and the mixture was stirred at room temperature for 16 h. The resulting suspension was washed with saturated $NaHCO_3$ solution (2 × 100 mL), and the organic layer dried with $MgSO_4$, filtered and concentrated in vacuo. Purification by column chromatography (SiO_2; eluent: hexane/EtOAc 9/1; by-product **6a**, $R_f = 0.23$; **5a**, $R_f = 0.05$). Recrystallisation of **5a** from hexane at 0 °C afforded pure **5a** as yellow needles (3.15 g, 66%). $T_{cl} = 119–121$ °C. ^{1}H NMR ($CDCl_3$): $\delta = 14.28$ (s, 1H, NH′CO); 9.25 (dd, 1H, H-4′); 8.33 (dd, 1H, H-6′); 8.00 (dd, 1H, H-6); 7.32 (dd, 1H, H-5′); 7.25 (s, 2H, *ortho*-H); 7.12 (m, 2H, H-4 and H-5); 6.56 (brs, 2H, NH_2); 4.07 (m, 6H, OCH_2); 1.88 (m, 6H, OCH_2CH_2); 1.49 (qui, 6H, $OCH_2CH_2CH_2$); 1.32 (brs, 12H, $(CH_2)_2$); 0.88 (t, 9H, CH_3). Anal. calcd. for $C_{35}H_{50}N_4O_4$ (MW 590.80): C 71.15, H 8.53, N 9.48. Found: C 71.3, H 8.3, N 9.3.

3,3′-Bis(3,4,5-trihexyloxybenzoylamino)-2,2′-bipyridine (6a): Compound **6a** ($R_f = 0.23$) from the preparation of **5a** (vide supra) was isolated and an analytically pure sample was obtained after recrystallisation from CH_2Cl_2/MeOH 8/2. K 53 °C M 110 °C I. IR (nujol): $\tilde{\nu} = 2928$ (C–H), 2856 (C–H), 1668 (C=O), 1578, 1459, 1375, 1333, 1225, 1112 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 14.15$ (s, 2H, NH); 9.40 (dd, 2H, H-4); 8.38 (dd, 2H, H-6); 7.50 (dd, 2H, H-5); 7.25 (s, 4H, *ortho*-H); 4.05 (m, 12H, OCH_2); 1.80 (m, 12H, OCH_2CH_2); 1.50 (qui, 12H, $OCH_2CH_2CH_2$); 1.31 (brs, 24H, $(CH_2)_2$); 0.88 (t, 18H, CH_3). Anal. calcd. for $C_{60}H_{90}N_4O_8$ (MW 995.39): C 72.39, H 9.11, N 5.63. Found: C 72.6, H 9.3, N 5.7.

***N,N′,N″*-Tris{[3(3′-(3,4,5-trihexyloxybenzoylamino)-2,2′-bipyridyl]}benzene-1,3,5-tricarbonamide (1a)**: A solution of 1,3,5-benzenetricarbonyl trichloride (0.29 g, 1.12 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise under an Ar atmosphere to a solution of **5a** (2 g, 3.39 mmol) and TEA (0.75 mL) in dry CH_2Cl_2 (40 mL). After 16 h of stirring at room temperature, the precipitate was filtered (P4 glass filter) and washed extensively with a mixture of acetone/$CHCl_3$ 1/1 yielding pure **1a** as a white sticky solid (1.79 g, 82%). $T_{cl} = 383$ °C (decomp.). IR (nujol): $\tilde{\nu} = 2892$ (C–H), 1668 (C=O), 1572, 1459, 1375, 1291, 1243, 1112 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 15.51$ (s, 3H, NHCO); 14.38 (s, 3H, NH′CO); 9.59 (d, 3H, H-4); 9.40 (d, 3H, H-4′); 9.25 (s, 3H, *ortho*-H); 9.04 (d, 3H, H-6′); 8.44 (d, 3H, H-6); 7.50 (dd, 6H, H-5 and H-5′); 7.26 (s, 6H, *ortho*-H′); 4.02 (m, 18H, OCH_2); 1.80 (qui, 18H, OCH_2CH_2); 1.51 (qui, 18H, $OCH_2CH_2CH_2$); 1.32 (m, 36H, $(CH_2)_2$); 0.88 (t, 27H, CH_3). Anal. calcd. for $C_{114}H_{150}N_{12}O_{15}$ (MW 1928.50): C 71.00, H 7.84, N 8.71. Found: C 70.9, H 7.3, N 8.6.

Methyl 3,4,5-tridodecyloxybenzoate (2b): A mixture of methyl 3,4,5-trihydroxybenzoate (3.5 g, 19 mmol), 1-bromododecane (14.5 g, 57 mmol) and K_2CO_3 (13 g) was heated under reflux in cyclohexanone (160 mL) for 40 h. After cooling, the precipitate was removed, and the filtrate was concentrated in vacuo. The resulting brown solid residue was purified by column chromatography (flash SiO_2; eluent: petroleum ether (60–80)/EtOAc (96/4)). Pure **2b** was isolated as a white powder (12.6 g, 90%). An analytically pure sample was obtained after recrystallisation from EtOH (96%). M.p. 43.2–43.8 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.22$ (s, 2H, *ortho*-H); 4.03 (m, 6H, OCH_2); 3.88 (s, 3H, OCH_3); 1.80 (m, 6H, OCH_2CH_2); 1.48 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 48H, $(CH_2)_8$); 0.90 (t, 9H, CH_3). Anal.calcd. for $C_{44}H_{80}O_5$ (MW 689.11): C 76.70, H 11.70. Found: C 77.3, H 11.8.

3,4,5-Tridodecyloxybenzoic acid (3b): A solution of KOH (0.9 g) in EtOH (96%, 28 mL) was added dropwise to a mixture of **2b** (5 g, 7.25 mmol) in EtOH (96%, 50 mL). The mixture was heated under reflux for 4 h. After cooling and acidification with a conc. HCl solution to pH = 2–3, the reaction mixture was poured into water (200 mL). The resulting white precipitate was filtered and recrystallised from EtOH (96%) to yield pure **3b** as a white powder (4 g, 82%). M.p. 57.5–58 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.31$ (s, 2H, *ortho*-H); 4.02 (m, 6H, OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.46 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 48H, $(CH_2)_8$); 0.88 (t, 9H, CH_3). Anal. calcd. for $C_{43}H_{78}O_5$ (MW 675.10): C 76.50, H 11.65. Found: C 77.2, H 11.7.

3,4,5-Tridodecyloxybenzoyl chloride (4b): Compound **3b** (2 g, 2.96 mmol) was treated with thionyl chloride (10 mL) under reflux for 3 h. The excess thionyl chloride was distilled off, and the resulting solid flushed with hexane (2 × 10 mL) to give pure **4b** as a white solid in quantitative yield (2.07 g, 100%).^{1}H NMR ($CDCl_3$): $\delta = 7.32$ (s, 2H, *ortho*-H); 4.05 (m, 6H, OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.46 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 48H, $(CH_2)_8$); 0.88 (t, 9H, CH_3).

3′-(3,4,5-Tridodecyloxybenzoylamino)-2,2′-bipyridine-3-amine (5b): A solution of **4b** (1.8 g, 2.6 mmol) in dry diethyl ether (20 mL) was added dropwise under an Ar atmosphere to an ice-cooled solution of 2,2′-bipyridine-3,3′-diamine (0.5 g, 2.6 mmol) and TEA (0.5 mL) in dry diethyl ether (25 mL). After complete addition, the ice bath was removed, and the mixture stirred at room temperature for 4 h. The mixture was concentrated in vacuo and purified by column chromatography (SiO_2; eluent: $CHCl_3$; $R_f = 0.55$ for by-product **6b** and $R_f = 0.28$ for **5b**) yielded pure **5b** as a yellow powder (1.27 g, 58%). Recrystallisation from hexane yielded an analytically pure sample. $T_{cl} = 64–65$ °C. ^{1}H NMR ($CDCl_3$): $\delta = 14.28$ (s, 1H, NH′CO); 9.25 (dd, 1H, H-4′); 8.33 (dd, 1H, H-6′); 8.00 (dd, 1H, H-6); 7.32 (dd, 1H, H-5′); 7.25 (s, 2H, *ortho*-H); 7.12 (m, 2H, H-4 and H-5); 6.56 (brs, 2H, NH_2); 4.07 (m, 6H, OCH_2); 1.88 (m, 6H, OCH_2CH_2); 1.49 (qui, 6H, $OCH_2CH_2CH_2$); 1.32 (brs, 48H, $(CH_2)_8$); 0.88 (t, 9H, CH_3). Anal. calcd. for $C_{53}H_{86}N_4O_4$ (MW 843.28): C 75.48, H 10.28, N 6.64. Found: C 75.8, H 10.2 , N 6.6.

3,3′-Bis(3,4,5-tridodecyloxybenzoylamino)-2,2′-bipyridine (6b): Compound **6b** ($R_f = 0.55$) from the preparation of **5b** (vide supra) was isolated, and an analytically pure sample obtained after recrystallisation from EtOAc. K 38 °C M 110 °C I. IR (nujol): $\tilde{\nu} = 2928$ (C–H), 2856 (C–H), 1656 (C=O), 1572, 1459, 1369, 1333, 1225, 1123 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 14.11$ (s, 2H, NH); 9.35 (dd, 2H, H-4); 8.38 (dd, 2H, H-6); 7.44 (dd, 2H, H-5); 7.25 (s, 4H, *ortho*-H); 4.05 (m, 12H, OCH_2); 1.85 (qui, 8H, *meta*-OCH_2CH_2); 1.77 (qui, 4H, *para*-OCH_2CH_2); 1.50 (qui, 12H, $OCH_2CH_2CH_2$); 1.31 (brs, 96H, $(CH_2)_8$); 0.88 (t, 18H, CH_3). Anal. calcd. for $C_{96}H_{162}N_4O_8$ (MW 1500.36): C 76.85, H 10.88, N 3.73. Found: C 76.4, H 11.1, N 3.4.

***N,N′,N″*-Tris{[3(3′-(3,4,5-tridodecyloxybenzoylamino)-2,2′-bipyridyl]}benzene-1,3,5-tricarbonamide (1b)**: A solution of 1,3,5-benzenetricarbonyl trichloride (0.13 g, 0.48 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a solution of **5b** (1.27 g, 1.5 mmol) and TEA (0.3 mL) in dry CH_2Cl_2 (15 mL). The mixture was heated under reflux for 18 h and, after cooling, concentrated in vacuo. To remove the salts, the solids were triturated with MeOH (2 × 20 mL). After purification with column chromatography (SiO_2, eluent: $CHCl_3$, $R_f = 0.50$) the oil was dissolved in $CHCl_3$ (20 mL) and cooled (0 °C). Acetone (15 mL) was added dropwise until a white solid precipitated. The precipitates were filtered and washed with acetone to yield pure **1b** as a sticky solid (0.76 g, 56%). $T_{cl} = 368$ °C. IR (nujol): $\tilde{\nu} = 2911$ (C–H), 1668 (C=O), 1579, 1502, 1377, 1300, 1250, 1111 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 15.49$ (s, 3H, NHCO); 14.36 (s, 3H, NH′CO); 9.56 (d, 3H, H-4); 9.38 (d, 3H, H-4′); 9.16 (s, 3H, *ortho*-H); 9.03 (d, 3H, H-6′); 8.38 (d, 3H, H-6); 7.52 (dd, 3H, H-5); 7.48 (dd, 3H, H-5′); 7.26 (s, 6H, *ortho*-H′); 4.05 (m, 18H, OCH_2); 1.85 (qui, 18H, OCH_2CH_2); 1.50 (qui, 18H, $OCH_2CH_2CH_2$); 1.31 (brs, 144H, $(CH_2)_8$); 0.88 (t, 27H, CH_3). Anal. calcd. for $C_{168}H_{258}N_{12}O_{15}$ (MW 2685.90): C 75.12, H 9.68, N 6.25. Found: C 75.1, H 9.6, N 6.2.

Methyl 3,4,5-trioctadecyloxybenzoate (2c): A mixture of methyl 3,4,5-trihydroxybenzoate (5 g, 27.15 mmol), 1-bromooctadecane (29 g) and anhydrous K_2CO_3 (20 g) was stirred under an Ar atmosphere in dimethylformamide/tetrahydofuran 1/1 (200 mL) at 80 °C for 24 h. The reaction mixture was allowed to cool to room temperature, poured into water (200 mL), and the precipitate was filtered and washed with toluene (100 mL). The product was used without further purification (11.65 g, 91%). An analytical pure sample was obtained by recrystallisation from diethyl ether. M.p. 61–63 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.25$ (s, 2H, *ortho*-H); 4.03 (m, 6H, OCH_2); 3.88 (s, 3H, OCH_3); 1.80 (m, 6H, OCH_2CH_2); 1.48 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 84H, $(CH_2)_{14}$); 0.90 (t, 9H, CH_3). Anal.calcd. for $C_{62}H_{116}O_5$ (MW 941.59): C 79.08, H 12.41. Found: C 79.2, H 12.4.

3,4,5-Trioctadecyloxybenzoic acid (3c) : A mixture of **2c** (5.75 g, 6.1 mmol) and KOH (2 g) was heated under reflux in EtOH (96%)/dioxane 1/1 (200 mL) for 4 h. After cooling and acidification with conc. HCl solution to pH = 2–3, the resulting white precipitate was filtered and washed with EtOH. After recrystallisation from EtOAc pure **3c** was obtained as a white powder (4.66 g, 82%). M.p. 86.5–87.2 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.31$ (s, 2H, *ortho*-H); 4.02 (m, 6H, OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.46 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 84H, $(CH_2)_{14}$); 0.88 (t, 9H, CH_3). Anal. calcd. for $C_{61}H_{114}O_5$ (MW 927.56): C 78.99, H 12.38. Found: C 79.1, H 12.7.

3,4,5-Trioctadecyloxybenzoyl chloride (4c): Compound **3c** (2.05 g, 5.39 mmol) was treated with thionyl chloride (40 mL) under reflux for 3 h. The excess thionyl chloride was distilled off and the resulting solid was flushed with hexane (2 × 10 mL) to give pure **4c** as a white solid in quantitative yield (2.1 g, 100%).^{1}H NMR ($CDCl_3$): $\delta = 7.32$ (s, 2H, *ortho*-H); 4.05 (m, 6H, OCH_2); 1.80 (m, 6H, OCH_2CH_2); 1.46 (qui, 6H, $OCH_2CH_2CH_2$); 1.30 (brs, 84H, $(CH_2)_{14}$); 0.88 (t, 9H, CH_3).

3′-(3,4,5-Trioctadecyloxybenzoylamino)-2,2′-bipyridine-3-amine (5c): A solution of **4c** (2.45 g, 2.6 mmol) in dry THF (40 mL) was added dropwise under an Ar atmosphere to an ice-cooled solution of 2,2′-bipyridine-3,3′-diamine (0.5 g, 2.6 mmol) and TEA (0.5 mL) in dry THF (80 mL). After complete addition, the mixture was stirred at room temperature for another 16 h. The mixture was poured into H_2O (100 mL) and extracted with diethyl ether (3 × 100 mL). The solvent was removed in vacuo, and the crude product recrystallised from CH_2Cl_2 yielding **5c** with a purity of 95% (the impurity is the diacylated compound) (2.18 g, 74%). Due to solubility difficulties, no further purification was attempted, and the compound was used as such. ^{1}H NMR ($CDCl_3$): $\delta = 14.22$ (s, 1H, NH′CO); 9.25 (dd, 1H, H-4′); 8.33 (dd, 1H, H-6′); 8.00 (dd, 1H, H-6); 7.32 (dd, 1H, H-5′); 7.25 (s, 2H, *ortho*-H); 7.12 (m, 2H, H-4 and H-5); 6.56 (brs, 2H, NH_2); 4.07 (m, 6H, OCH_2); 1.88 (m, 6H, OCH_2CH_2); 1.49 (qui, 6H, $OCH_2CH_2CH_2$); 1.32 (brs, 84H, $(CH_2)_{14}$); 0.88 (t, 9H, CH_3).

***N,N′,N″*-Tris{[3(3′-(3,4,5-trioctadecyloxybenzoylamino)-2,2′-bipyridyl]}benzene-1,3,5-tricarbonamide (1c)**: A solution of 1,3,5-benzenetricarbonyl trichloride (60 mg, 0.22 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise under an Ar atmosphere to a solution of **5c** (0,85 g, 0.68 mmol) and TEA (0.15 mL) in dry CH_2Cl_2 (40 mL). The mixture was heated under reflux for 16 h. The white precipitate was filtered off (P4 glass filter) and washed with cold CH_2Cl_2. The crude product was purified by column chromatography (SiO_2). The impurities were eluted with CH_2Cl_2 (**1c** hardly dissolves in CH_2Cl_2 at room temperature). Extensive elution with $CHCl_3$ yielded **1c**. After evaporation of the solvent, compound **1c** was dissolved in $CHCl_3$, (15 mL) and the solution cooled (0 °C). Acetone was slowly added until a white solid precipitated. The precipitate was filtered and washed with acetone to yield **1c** as a white powder (0.46 g, 54%). $T_{cl} = 308$ °C (decomp.). IR (nujol): $\tilde{\nu} = 2926$ (C–H), 2856 (C–H), 1668 (C=O), 1578, 1459, 1375, 1303 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 15.49$ (s, 3H, NHCO); 14.39 (s, 3H, NH′CO); 9.55 (d, 3H, H-4); 9.40 (d, 3H, H-4′); 9.22 (s, 3H, *ortho*-H); 9.04 (d, 3H, H-6′); 8.42 (d, 3H, H-6); 7.55 (dd, 3H, H-5); 7.49 (dd, 3H, H-5′); 7.26 (s, 6H, *ortho*-H′); 4.05 (m, 18H, OCH_2); 1.85 (qui, 18H, OCH_2CH_2); 1.50 (qui, 18H, $OCH_2CH_2CH_2$); 1.31 (brs, 252H, $(CH_2)_{14}$); 0.88 (t, 27H, CH_3). Anal. calcd. for $C_{222}H_{366}N_{12}O_{15}$ (MW 3443.40): C 77.43, H 10.71, N 4.88. Found: C 77.3, H 10.7, N 5.1.

***N,N′,N″*-Trisphenyl-1,3,5-benzenetricarbonamide (7)**: A solution of 1,3,5-benzenetricarbonyl trichloride (1 g, 3.76 mmol) in dry CH_2Cl_2 (15 mL) was added slowly to an ice-cooled mixture of aniline (1.1 g, 11.4 mmol) and TEA (1.7 mL) in dry CH_2Cl_2 (25 mL). After 2 h of stirring, the ice bath was removed, and the stirring continued at room temperature for another 12 h. MeOH (25 mL) was added to the clear solution. The resulting white precipitate was filtered and washed thoroughly with MeOH and, after drying, pure **7** was obtained as a white powder (1.23 g, 72%). M.p. 327–329 °C. ^{1}H NMR ([D_7]DMF): $\delta = 10.65$ (s, 3H, NHCO); 8.81 (s, 3H, *ortho*-H); 7.98 (d, 6H, *ortho*-H′); 7.45 (t, 6H, *meta*-H′); 7.19 (t, 3H, *para*-H′). FAB-MS: *m/z* (%): 436 (100) $[M+H]^+$; 458 (28) $[M+Na]^+$.

3′-*tert*-Butoxycarbonylamino-2,2′-bipyridine-3-amine (10): A mixture of 3,3′-diamino-2,2-bipyridine (0.80 g, 4.3 mmol) and Boc_2O (0.95 g, 4.3 mmol) in dry THF (30 mL) was heated under reflux for 18 h. After the solution had been cooled to room temperature, it was poured into water (200 mL) and stirred for 10 min. The water phase was extracted with diethyl ether (3*100 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. The resulting yellow oil was purified by column chromatography. The diacylated by-product was eluted (eluent: hexane/EtOAc 95/5, $R_f = 0.12$). Then, the desired monoacylated compound **10** was eluted (eluent: $CHCl_3/CH_3CN$/hexane 1.8/2.5/3, $R_f = 0.6$). After evaporation of the solvent in vacuo, pure **10** was obtained as a yellow oil (0.87 g, 70%). ^{1}H NMR ($CDCl_3$): $\delta = 12.42$ (s, 1H, NHCO); 8.76 (d, 1H, H-4);8.24 (d, 1H, H-6); 8.02 (d, 1H, H-6′); 7.23 (dd, 1H, H-5); 7.10 (m, 2H, H-5′ and H-4′); 6.35 (brs, 2H, NH_2); 1.53 (s, 9H, $C(CH_3)_3$).

***N,N′,N″*-Tris[3(3′-t-butoxycarbonylamino-2,2′-bipyridyl)]benzene-1,3,5-tricarbonamide (9)**: A solution of 1,3,5-benzenetricarbonyl trichloride (0.39 g, 1.5 mmol) was added slowly to an ice-cooled solution of **10** (1.40 g, 4.8 mmol) and TEA (0.7 mL) in dry THF (50 mL). The reaction was carried out under an Ar atmosphere. After complete addition, the ice bath was removed and the mixture stirred at room temperature for another 18 h. The resulting white precipitate was filtered and washed with cold THF (3 × 5 mL), H_2O (3 × 10 mL) and saturated $NaHCO_3$ solution (2 × 10 mL). The resulting white solid was suspended in MeOH to remove last traces of TEA·HCl. After filtration and drying of the residue, pure **9** was obtained as a white powder (1.36 g, 83%). M.p. 265 °C (decomp.).^{1}H NMR ($CDCl_3$): $\delta = 15.33$ (s, 3H, NHCO); 12.77 (s, 3H, NHBoc); 9.44 (d, 3H, H-4); 9.10 (s, 3H, *ortho*-H); 8.90 (m, 6H, H-6 and H-4′); 8.38 (d, 3H, H-6′); 7.41 (m, 6H, H-5 and H-5′); 1.57 (s, 27H, $C(CH_3)_3$). FAB-MS: *m/z* (%): 1037 (42) $[M+Na]^+$; 1015 (83) $[M+H]^+$; 941 (52) $[M+H-C(CH_3)_3O]^+$; 914 (55) $[M+H-C(CH_3)_3OCO]^+$.

***N,N′,N″*-Tris[3(3′-amino-2,2′-bipyridyl)]benzene-1,3,5-tricarbonamide (8)**: TFA (10 mL) was added carefully to a solution of **9** (1.00 g, 1 mmol) in CH_2Cl_2 (10 mL). The yellow solution was stirred for 18 h at room temperature. Then, TEA (10 mL) was cautiously added through a dropping funnel (this addition gave rise to aggressive fumes). The resulting yellow precipitate was filtered, washed with CH_2Cl_2/TEA (1/1, 3 × 5 mL) and suspended in CH_2Cl_2 (20 mL). After filtration and drying of the precipitate, **8** was obtained as a yellow powder which, owing to solubility problems, was used without further purification (0.7 g, 99%). M.p. 167 °C (decomp.). ^{1}H NMR ([D_7]DMF): $\delta = 15.79$ (s, 3H, NHCO); 9.46 (dd, 3H, H-4); 9.23 (s, 3H, *ortho*-H); 8.60 (dd, 3H, H-6′); 8.50 (dd, 3H, H-6); 7.77 (brs, 6H, NH_2); 7.51 (dd, 3H, H-5′); 7.47 (dd, 3H, H-4′); 7.32 (dd, 3H, H-5).

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[7] Initial efforts to synthesise disc-shaped derivative **1b** were based on a divergent approach. Therefore, a selective monoacylation of 2,2′-bipyridine-3,3′-diamine with Boc_2O was developed. Unfortunately, after coupling of the Boc-monoprotected 2,2′-bipyridine-3,3′-diamine with benzene-1,3,5-tricarbonyl trichloride and removal of the Boc group, a sparingly soluble triamine was obtained that could only be coupled with acid chloride **4b** in low yields (5%).

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[10] The diacylated compounds **6a,b** were also isolated and purified. A full characterisation of these compounds is included in the Experimental Section. As expected, they also show liquid crystalline behaviour. Preliminary X-ray results suggest that a D_{ho} phase is present in both compounds.

[11] Compounds **1b–c** also show a concentration effect. Owing to their high molecular weights, the effect of change in concentration by weight is less pronounced than for **1a**. Therefore, only the effects of concentration and temperature variations relating to **1a** are discussed.

[12] Full details dealing with gel formation will be published elsewhere.

[13] The differences in the clearing temperatures obtained by DSC and polarisation microscopy are due to inefficient heat transfer at high temperatures in the heating element of the microscope.