Areno-Condensed 1,7,13-Triaza[18]annulenes

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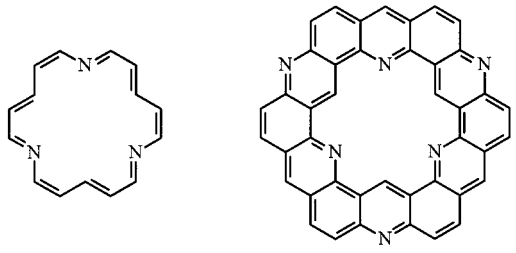
The 1,7,13-triaza[18]annulenes **9a–c** were prepared by multistep processes in which the final step consisted of a threefold cyclic condensation reaction of the Schiff bases **8a–c**. Due to the length of the nine peripheral alkoxy chains, discotic liquid crystalline phases were obtained for **9b,c**. The three nitrogen atoms in the central 18-membered ring not only permit protonation, but they can also serve for the complexation of NH_4^+ ions. The compounds **9a–c** are highly photosensitive and exhibit crosslinking reactions on irradiation.

Introduction

Areno-condensed [n]annulenes ($n \geq 12$) are thermally stable disc-like compounds[1−15] that exhibit valuable properties for applications in materials science — for example for photoconducting columnar liquid crystals or for imaging and data-storage techniques with liquid crystal (LC) phases.[3,4,8,9,11] [18]Annulenes condensed with three naphthalene, phenanthrene, chrysene or pyrene ring systems have proven to be particularly suitable for the generation of discotic LC phases that exist over very broad temperature intervals. Moreover, several areno-condensed annulenes show an interesting photochemistry.[3,4,6−8,10,11,14,15]

We are now studying the synthesis and properties of areno-condensed 1,7,13-triaza[18]annulenes. The parent system **1** (Scheme 1) and derivatives of it are unknown; a remote relation can only be seen to hexaazakekulene **2**,[16] which contains the corresponding 18-membered ring as an inner perimeter.



1 **2**

Scheme 1. 1,7,13-Triaza[18]annulene **1** and the related hexaazakekulene **2**

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Results and Discussion

The preparation of the target compounds began with a condensation reaction of 2-cyanomethyl-6-methyl-pyridine (**3**)[17,18] and 3,4,5-trialkoxybenzaldehydes **4a−c**[12,19] in piperidine. The obtained stilbazoles **5a−c** were irradiated with a medium-pressure mercury lamp, so that the (*Z*)-configuration was partly transformed to the (*E*)-configuration **5′a−c**, which entered into a reversible photocyclisation ([6π] electrocyclic ring closure). The intermediate *trans*-4a,4b-dihydrobenzo[*f*]quinolines were irreversibly dehydrogenated in situ to the heteroaromatics **6a−c**.[20−22] The following step consisted of a replacement of the cyano group by a formyl group, achieved by reduction with DIBAL-H. The yields of the aldehydes **7a−c** were rather modest; however, the subsequent generation of the Schiff bases **8a−c** proved to be a quantitative step and, moreover, it was not necessary to isolate these compounds. The annulenes **9a−c** could therefore be obtained from the aldehydes **7a−c** in a one-pot reaction. The Siegrist reaction[23] **8a−c** → **9a−c** has an enormously high *trans* selectivity.[23,24] The threefold cyclic condensation still has to compete with linear processes. However, since the linear oligomers contain polar end groups they can easily be removed by column chromatography.

Compound **9a** forms crystals which start to decompose above 200 °C; the derivatives with the longer alkoxy chains exist in liquid crystalline phases at room temperature. Since **9b** proved to be very sensitive towards daylight, the study of the mesophase was performed with **9c**. Differential scanning calorimetry (Figure 1) shows a broad peak with a maximum at −2.8 °C which can be assigned to the melting of the dodecyloxy chains. The transition to the LC phase occurs at 19.5 °C and the clearing point is reached at 156.6 °C. These data refer to the second heating curve and represent maxima of sharp peaks which were obtained with a heating rate of 10 K min^{-1}. The same rate in the subsequent cooling curve leads to an LC phase between 150.2 and −4.6 °C.

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Both transitions exhibit an undercooling effect. A comparison between **9c** and **9c′**,[9,10,12] in which the pyridine rings of **9c** are replaced by benzene rings (Scheme 2), reveals a narrowing of the temperature interval for the mesophase of **9c**; the clearing point of **9c′** is at 230 °C.[12] The texture of **9c** measured on a polarizing microscope is very similar to the texture of the corresponding triphenanthro[18]annulene **9c′**. Therefore a Col_h phase can be assumed for both **9c** and **9c′**. The photosensitivity is much higher for **9c** than for **9c′**, particularly at temperatures above 100 °C; even the unfiltered light of the polarization microscope leads to a degradation of the LC phase. Both systems are suitable for irreversible imaging techniques.

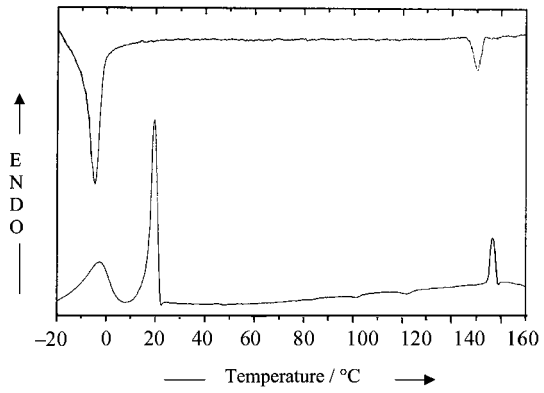
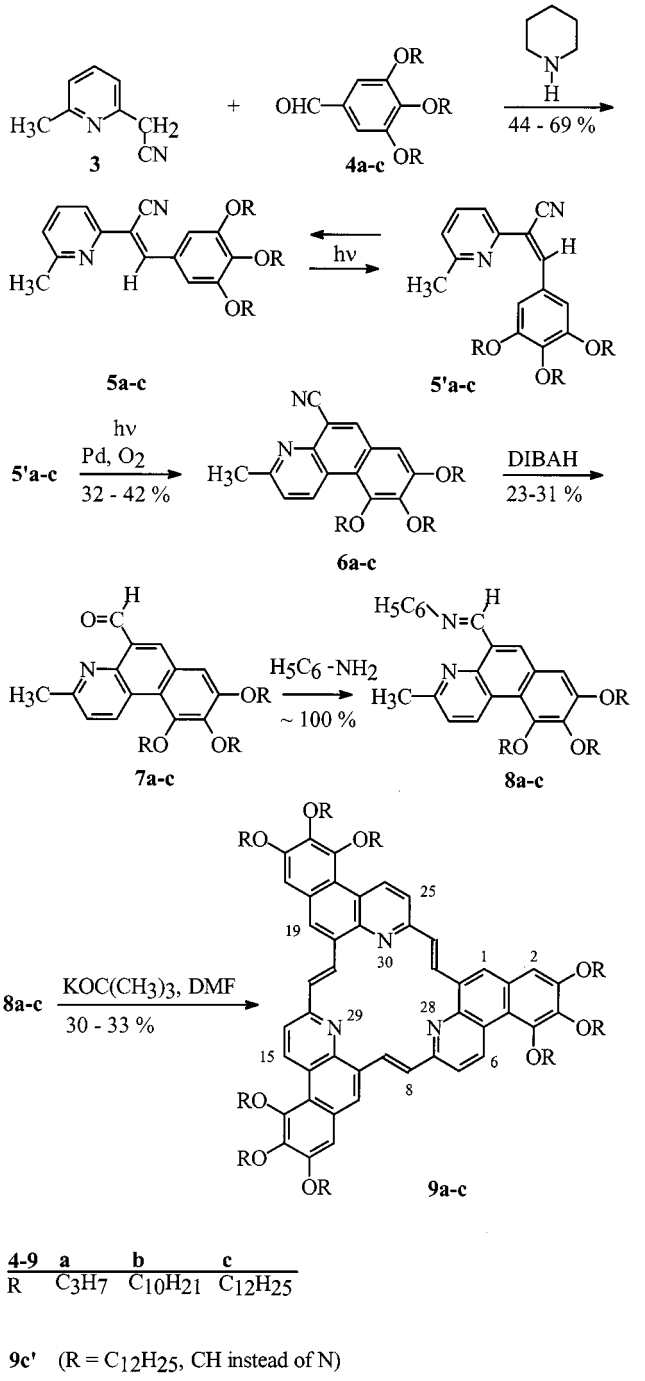


Figure 1. Second heating and cooling curve in the differential scanning calorimetry of compound **9c**

The UV/Vis spectrum of **9c** in *n*-hexane contains an intense maximum at λ_{max} = 368 nm (ε_{max} = 56100) with shoulders at λ_{max} = 395 nm (ε_{max} = 33200) and λ_{max} = 417 nm (ε_{max} = 17900). Further maxima are located at λ_{max} = 241 nm (ε_{max} = 27400), λ_{max} = 295 nm (ε_{max} = 24100) and λ_{max} = 320 nm (ε_{max} = 29200). Figure 2 shows the reaction spectra for monochromatic irradiation (λ = 366 nm) of **9c**. Interestingly the shape of the absorption curve is widely preserved, although the relative intensities of the transitions change significantly. One can assume three vinylazaphenanthrene chromophores in **9** which are more or less independent from each other because of the noncoplanarity of the molecule.[4] The reaction spectra in Figure 2 indicate that only a certain part of the vinylazaphenanthrene chromophores react. This process is fast in the beginning and then it slows down. In contrast to the cyclophane formation of the carbocyclic analogues,[9,10] photocrosslinking to oligomers predominates here. Due to steric reasons the *trans* → *cis* photoisomerization is not an important process for either **9c** or **9c′**.

The ^{1}H NMR spectra of **9a**–**c** in deuterated chloroform show two singlets and two AB spin patterns at low field (Table 1). The inner protons 9-H, 18-H and 27-H have higher δ values than the outer protons 8-H, 17-H and 26-H. The same observation was made for carbocyclic systems similar to **9c′**; however, due to the influence of the nitrogen



Scheme 2. Preparation of the areno-condensed triaza[18]annulenes **9a**–**c**

atoms the differences (Δδ) for the chemical shifts of the olefinic protons are higher in the heterocyclic series. One can consider the compounds **9a**–**c** as consisting of heteroaromatic "islands" which are connected by *trans*-configured olefinic bridges. A macrocyclic ring current does not exist. Protonation with an excess of trifluoroacetic acid leads to a low-field shift for almost all the ^{1}H NMR signals, except for the olefinic protons, where the signal for the outer protons H_o remains constant, and the signal for the inner protons H_i is shifted by about 0.3 ppm to higher field.

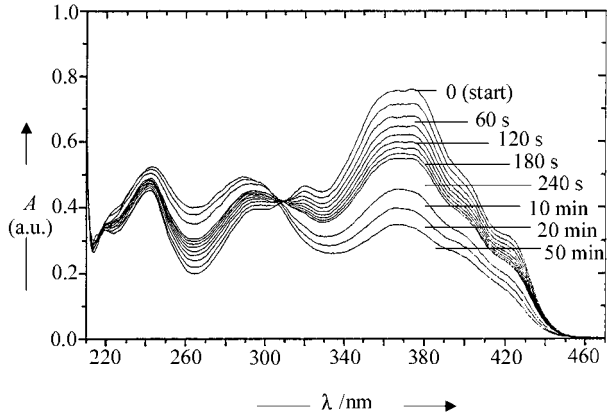


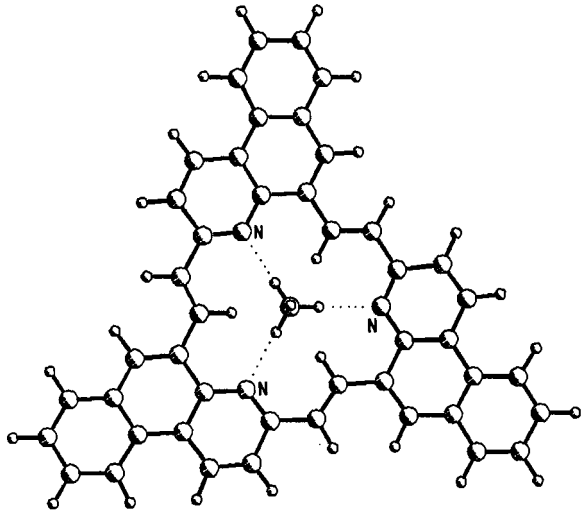
Figure 2. UV/Vis reaction spectra of the monochromatic irradiation (λ = 366 nm) of compound **9c** in *n*-heptane

Table 1. ^{1}HMR data of **9a**−**c** in $CDCl_3$

	9a		**9b**		**9c**	
	δ	^3J [Hz]	δ	^3J [Hz]	δ	^3J [Hz]
1-H (s)	8.44		8.46		8.44	
2-H (s)	7.19		7.19		7.17	
6-H (d)	9.90	8.8	9.91	8.8	9.90	8.8
7-H (d)	7.56	8.8	7.57	8.8	7.56	8.8
8-H (d)[a]	7.69	16.1	7.71	16.1	7.68	16.1
9-H (d)[a]	9.79	16.1	9.83	16.1	9.81	16.1

[a] Assignment by NOE measurements.

A completely different situation is found when a solution of $NH_4^+PF_6^-$ in CD_3OD is added to the solution of **9c** in $CDCl_3$. All ^{1}H NMR signals become broad and structureless and are found at higher field. The range of the signals of the aromatic and olefinic protons is shifted from δ = 7.17−9.81 to δ = 5.50−9.70. Obviously the NH_4^+ ions form a complex with the triaza[18]annulene ring, and it seems reasonable that three hydrogen bonds are generated to the pyridine nitrogen atoms, whereas the fourth hydrogen of the ammonium ion may only be involved in an exchange mechanism. The result of a force field calculation[25] is shown in Scheme 3. The calculated average distance for the hydrogen bonds amounts to 195 pm. The complexation is completely reversible.



Scheme 3. Model for the complexation of areno-condensed 1,7,13-triaza[18]annulenes with ammonium ions[25]

Conclusion

The areno-condensed 1,7,13-triaza[18]annulenes **9a**−**c** can be obtained by a threefold cyclic condensation reaction of the *N*-phenylimines **8a**−**c** in a strongly alkaline medium. Long alkoxy side chains on the periphery of these molecules lead to the generation of discotic liquid crystalline phases over broad temperature intervals. The compounds **9a**−**c** are highly light-sensitive and show an irreversible photocrosslinking. Apart from the protonation, doping with ammonium ions is possible; a complexation of NH_4^+ with the formation of three hydrogen bonds to the N atoms of the annulene ring has to be assumed.

Experimental Section

General Remarks: Melting points (uncorrected): Büchi apparatus. NMR: Bruker AM 400, $CDCl_3$ as solvent unless otherwise stated, TMS as internal standard. MS: Varian MAT CH7A and Finnigan MAT 95. UV/Vis: Zeiss MCS 320/340, *n*-heptane or *n*-hexane as solvent. IR: Beckman Acculab 4, measurement in KBr or neat. DSC: Perkin−Elmer DSC-7. Polarization microscopy: Leitz Ortholux II Pol-BK/Mettler FP 52.

General Procedure for the Preparation of the (*Z*)-Configured Olefins 5a−c: 2-Cyanomethyl-6-methylpyridine (**3**)[17,18] (13.5 g, 48.2 mmol), 3,4,5-trialkoxybenzaldehyde (**4a**−**c**; 48.2 mmol)[12,19] and piperidine (3 mL, 30.3 mmol) were refluxed in 100 mL of ethanol for 3 h. After 12 h at 5 °C, the formed precipitate was collected and recrystallized twice from methanol or ethanol.

2-[1-Cyano-2-(3,4,5-tripropoxyphenyl)ethenyl]-6-methylpyridine (5a): Yield 8.37 g (44%) of a yellow fluorescing solid, m.p. 66 °C. IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 2212, 1585, 1504, 1453, 1433, 1330, 1257, 1124, 793. ^{1}H NMR ($CDCl_3$): δ = 1.00−1.15 (m, 9 H, CH_3), 1.70−1.95 (m, 6 H, CH_2), 2.59 (s, 3 H, CH_3), 4.01 (m, 6 H, OCH_2), 7.09 (d, 1 H, 5-H), 7.26 (s, 2 H, aromat. H), 7.51 (d, 1 H, 3-H), 7.64 (dd, 1 H, 4-H), 8.37 (s, 1 H, olefin. H). ^{13}C NMR ($CDCl_3$): δ = 10.5, 10.6 (CH_3), 22.6, 23.6 (CH_2), 24.7 (6-CH_3), 70.7, 75.2 (OCH_2), 108.5 (olefin. C_q), 108.7 (aromat. CH), 118.2, 122.9, 137.4 (CH, pyridine), 118.5 (CN), 128.4 (aromat. C_q), 140.9, 153.1 (C_qO), 145.1 (olefin. CH), 150.5, 158.6 (C_q, pyridine). EI-MS (70 eV): *m*/*z* (%) = 394 (100) [$M^{+\cdot}$], 352 (46), 267 (53). $C_{24}H_{30}N_2O_3$ (394.5): calcd. C 73.07, H 7.66, N 7.10; found C 72.91, H 7.66, N 7.06.

2-[1-Cyano-2-(3,4,5-tridecyloxyphenyl)ethenyl]-6-methylpyridine (5b): Yield 15.94 g (48%) of a yellow fluorescing solid, m.p. 59 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.26 (m, 36 H, CH_2), 1.48 (m, 6 H, CH_2), 1.75 (m, 2 H, CH_2), 1.82 (m, 4 H, CH_2), 2.58 (s, 3 H, CH_3), 4.03 (m, 6 H, OCH_2), 7.09 (d, 1 H, 5-H), 7.24 (s, 2

H, aromat. H), 7.51 (d, 1 H, 3-H), 7.62 (dd, 1 H, 4-H), 8.37 (s, 1 H, olefin. H). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 26.2, 29.4, 29.5, 29.6, 29.7, 29.8, 30.4, 32.0 (CH_2, partly superimposed), 24.7 (6-CH_3), 69.2, 73.6 (OCH_2), 108.4 (olefin. C_q), 108.6 (aromat. CH), 118.2, 122.9, 137.4 (CH, pyridine), 118.5 (CN), 128.4 (aromat. C_q), 104.9, 153.1 (C_qO), 145.0 (olefin. CH), 150.5, 158.5, (C_q, pyridine). EI-MS (70 eV): *m*/*z* (%) = 689 (49) [$M^{+\cdot}$] 548 (23), 267 (39), 57 (71), 43 (100). $C_{45}H_{72}N_2O_3$ (689.1): calcd. C 78.44, H 10.53, N 4.07; found C 78.14, H 10.41, N 3.95.

2-[1-Cyano-2-(3,4,5-tridodecyloxyphenyl)ethenyl]-6-methylpyridine (5c): Yield 75.71 g (69%) of a yellow-ochre solid, m.p. 67 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.25 (m, 54 H, CH_2), 1.78 (m, 6 H, CH_2), 2.58 (s, 3 H, CH_3), 4.03 (m, 6 H, OCH_2), 7.09 (d, 1 H, 5-H), 7.24 (s, 2 H, aromat. H), 7.51 (d, 1 H, 3-H), 7.62 (dd, 1 H, 4-H), 8.37 (s, 1 H, olefin. H). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.4, 29.6, 30.3, 31.9 (CH_2, partly superimposed), 24.6 (6-CH_3), 69.1, 73.6 (OCH_2), 108.3 (olefin. C_q), 108.5 (aromat. CH), 118.2, 122.9, 137.4 (CH, pyridine), 118.4 (CN), 128.3 (aromat. C_q), 140.9, 153.1 (CqO), 145.0 (olefin. CH), 150.5, 158.5 (C_q, pyridine). EI-MS (70 eV): *m*/*z* (%) = 773 (100) [$M^{+\cdot}$], 604 (20), 267 (27), 57 (28), 43 (24). $C_{51}H_{84}N_2O_3$ (773.2): calcd. C 79.22, H 10.95, N 3.62; found C 79.10, H 11.01, N 3.57.

General Procedure for the Preparation of the Azaphenanthrenes 6a−c: A solution of **3a−c** (6.0 mmol) in 180 mL of benzene and 1620 mL of *tert*-butyl alcohol was saturated with oxygen; 0.2 g palladium on coal was added and the mixture irradiated for 24 h with a Hanovia 450 W medium pressure lamp equipped with a Corex filter. During the irradiation a weak stream of oxygen was bubbled through the stirred solution. The filtered solution was evaporated and the residue recrystallized from ethanol. (TLC showed that some starting material was still present in the crude product; however, prolonged irradiation led to side products which could not be easily separated).

2-Methyl-5,6,7-tripropoxybenzo[*f*]quinoline-10-carbonitrile (6a): Yield 0.75 g (32%) of an ochre solid, m.p. 132 °C. IR (KBr): $\tilde{\nu}$ = 2931, 2223, 1603, 1457, 1363, 1266, 1176, 1089, 955 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.00−1.15 (m, 9 H, CH_3), 1.85−2.00 (m, 6 H, CH_2), 2.78 (s, 3 H, 2-CH_3), 4.05−4.12 (m, 6 H, OCH_2), 7.10 (s, 1 H, 8-H), 7.43 (d, ^3J = 9.0 Hz, 1 H, 3-H), 8.25 (s, 1 H, 9-H), 9.73 (d, ^3J = 9.0 Hz, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ = 10.6, 10.7, 10.7 (CH_3), 22.5, 22.5, 23.6 (CH_2), 24.9 (2-CH_3), 70.4, 75.4, 75.8 (OCH_2), 106.5 (C-8), 111.3 (C-10), 118.0 (CN), 120.3 (C-4b), 122.8 (C-3), 123.3, 127.1 (C-4a, C-8a), 135.0, 137.8 (C-4, C-9), 144.8, 145.0, 151.6, 153.3 (C-5, C-6, C-7, C-10a), 158.4 (C-2). EI-MS (70 eV): *m*/*z* (%) = 392 (78) [$M^{+\cdot}$], 308 (41), 266 (55), 265 (53), 151 (26), 137 (23), 125 (40), 123 (39), 111 (67), 109 (76), 95 (100). $C_{24}H_{28}N_2O_3$ (392.5): calcd. C 73.44, H 7.19, N 7.14; found C 73.44, H 7.19, N 7.14.

5,6,7-Tridecyloxy-2-methylbenzo[*f*]quinoline-10-carbonitrile (6b): Yield 1.36 g (33%) of a light-yellow solid, m.p. 70 °C. ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 9 H, CH_3), 1.26 (m, 42 H, CH_2), 1.87 (m, 6 H, CH_2), 2.79 (s, 3 H, 2-CH_3), 4.11 (m, 6 H, OCH_2), 7.09 (s, 1 H, 8-H), 7.43 (d, ^3J = 8.8 Hz, 1 H, 3-H), 8.25 (s, 1 H, 9-H), 9.72 (d, ^3J = 8.8 Hz, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.4, 31.9 (CH_2, partly superimposed), 24.9 (2-CH_3), 68.8, 73.9, 74.3 (OCH_2), 106.4 (C-8), 111.2 (C-10), 118.0 (CN), 120.2 (C-4b), 122.8 (C-3), 123.3, 127.1 (C-4a, C-8a), 135.0, 137.8 (C-4, C-9), 144.7, 145.0, 151.6, 153.3 (C-5, C-6, C-7, C-10a), 158.3 (C-2). EI-MS (70 eV): *m*/*z* (%) = 687 (100) [$M^{+\cdot}$], 406 (25), 266 (52), 57 (42), 43 (54). $C_{45}H_{70}N_2O_3$ (687.1): calcd. C 78.67, H 10.27, N 4.08; found C 78.67, H 10.29, N 4.08.

5,6,7-Tridodecyloxy-2-methylbenzo[*f*]quinoline-10-carbonitrile (6c): Yield 1.94 g (42%) of a yellowish solid, m.p. 74 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.25 (m, 54 H, CH_2), 1.87 (m, 6 H, CH_2), 2.79 (s, 3 H, 2-CH_3), 4.11 (m, 6 H, OCH_2), 7.09 (s, 1 H, 8-H), 7.43 (d, ^3J = 8.8 Hz, 1 H, 3-H), 8.25 (s, 1 H, 9-H), 9.72 (d, ^3J = 8.8 Hz, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.2, 29.4, 29.5, 29.6, 29.7, 30.4, 30.5, 31.9 (CH_2, partly superimposed), 24.9 (2-CH_3), 68.8, 73.9, 74.3 (OCH_2), 106.4 (C-8), 111.2 (C-10), 118.0 (CN), 120.2 (C-4b), 122.7 (C-3), 123.3, 127.1 (C-4a, C-8a), 134.9, 137.8 (C-4, C-9), 144.7, 145.0, 151.6, 153.3 (C-5, C-6, C-7, C-10a), 158.3 (C-2). FD-MS: *m*/*z* (%) = 771 (100) [$M^{+\cdot}$]. $C_{51}H_{82}N_2O_3$ (771.2): calcd. C 79.43, H 10.72, N 3.63; found C 79.30, H 10.59, N 3.63.

2-Methyl-5,6,7-tripropoxybenzo[*f*]quinoline-10-carbaldehyde (7a): 3 mL of a DIBAL-H solution (20% in toluene, 3.58 mmol) was added through a syringe to a cold solution (−50 °C) of **4a** (0.62 g, 1.58 mmol) in 30 mL of dry dichloromethane,. The reaction mixture became orange. After stirring for 30 min at −50 °C and a further 30 min during which the temperature was raised to −20 °C, 5 mL of methanol was added. The liquid phase was extracted with the same amount of water, aqueous NH_4Cl and saturated NaCl solution, dried with $MgSO_4$ and the solvents evaporated. The raw material was purified by column chromatography (30 × 3 cm SiO_2, CH_2Cl_2). Yield 195 mg (31%) of a yellow solid, m.p. 77 °C [from petroleum ether (b.p. 40−70 °C)]. IR (KBr): $\tilde{\nu}$ = 2967 cm^{-1}, 1684, 1605, 1453, 1361, 1266, 1089, 1043. ^{1}H NMR ($CDCl_3$): δ = 1.00−1.15 (m, 9 H, CH_3), 1.85−2.00 (m, 6 H, CH_2), 2.78 (s, 3 H, 2-CH_3), 4.00−4.20 (m, 6 H, OCH_2), 7.22 (s, 1 H, 8-H), 7.42 (d, ^3J = 9.2 Hz, 1 H, 3-H), 8.46 (s, 1 H, 9-H), 9.79 (d, ^3J = 9.2 Hz, 1 H, 4-H), 11.44 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ = 10.6, 10.7, 10.7 (CH_3), 22.6, 23.7, 23.7 (CH_2), 24.9 (2-CH_3), 70.3, 75.3, 75.8 (OCH_2), 108.0 (C-8), 121.4, 123.3, 127.5, 129.3 (C-4a, C-4b, C-8a, C-10), 121.7 (C-3), 131.5 (C-9), 135.1 (C-4), 144.8, 145.9, 151.5, 153.0 (C-5, C-6, C-7, C-10a), 157.0 (C-2), 193.8 (CHO). EI-MS (70 eV): *m*/*z* (%) = 395 (10) [$M^{+\cdot}$], 367 (100), 240 (17). $C_{24}H_{29}NO_4$ (395.5): calcd. C 72.89, H 7.39, N 3.54; found C 72.89, H 7.41, N 3.59.

5,6,7-Tridecyloxy-2-methylbenzo[*f*]quinoline-10-carbaldehyde (7b): The compound was prepared analogously to **7a**. Workup as described above yielded 23% of a yellowish solid which melted at 60 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.26 (m, 42 H, CH_2), 1.87 (m, 6 H, CH_2), 2.76 (s, 3 H, 2-CH_3), 4.11 (m, 6 H, OCH_2), 7.22 (s, 1 H, 8-H), 7.41 (d, ^3J = 8.9 Hz, 1 H, 3-H), 8.44 (s, 1 H, 9-H), 9.77 (d, ^3J = 8.9 Hz, 1 H, 4-H), 11.45 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.2, 29.3, 29.5, 29.6, 29.6, 29.7, 30.4, 30.5, 31.9 (CH_2, partly superimposed), 24.8 (2-CH_3), 68.7, 73.8, 74.2 (OCH_2), 108.0, (C-8), 121.3, 123.4, 127.5, 129.1 (C-4a, C-4b, C-8a, C-10), 121.4 (C-3), 131.7 (C-9), 135.2 (C-4), 144.9, 145.6, 151.5, 153.0 (C-5, C-6, C-7, C-10a), 156.9 (C-2), 193.7 (CHO). The NMR spectra showed some minor impurities, although the product could be used without further purification for the preparation of the target compound **9b**.

5,6,7-Tridodecyloxy-2-methylbenzo[*f*]quinoline-10-carbaldehyde (7c): Preparation and workup as described for **7a**. Yield 30% of an ochre solid which melted at 60 °C and was used for the following step without further purification. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.25 (m, 48 H, CH_2), 1.53 (m, 6 H, CH_2), 1.88 (m, 6 H, CH_2), 2.75 (s, 3 H, 2-CH_3), 4.11 (m, 6 H, OCH_2), 7.21 (s, 1 H, 8-H), 7.40 (d, ^3J = 8.8 Hz, 1 H, 3-H), 8.42 (s, 1 H, 9-H), 9.75 (d, ^3J = 8.8 Hz, 1 H, 4-H), 11.45 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.7, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.4, 30.5, 31.9 (CH_2, partly superimposed), 24.8 (2-CH_3), 68.8, 73.8,

74.2 (OCH_2), 108.1 (C-8), 121.3, 123.3, 127.5, 129.3 (C-4a, C-4b, C-8a, C-10), 121.6 (C-3), 131.4 (C-9), 135.0 (C-4), 144.9, 145.9, 151.5, 153.0 (C-5, C-6, C-7, C-10a), 156.9 (C-2), 193.5 (CHO).

General Procedure for the Preparation of the Tris(azaphenanthro)[18]annulenes 9a−c: The aldehydes **7a−c** (1.0 mmol) were treated with aniline (186 mg, 2.0 mmol) at 75 °C and 100 mbar for 6 h. The water generated during the formation of the Schiff bases **8a−c** was continuously removed. The excess aniline was then evaporated by reducing the pressure to 1 mbar. The residue was dissolved in 100 mL of DMF and the solution degassed with an argon stream. An excess of $KOC(CH_3)_3$ (1.12 g, 10.0 mmol) was then added under argon at 85 °C and the solution vigorously stirred for 10 min at this temperature. The reaction vessel was then cooled to 0 °C before 100 mL of ice-water was added so that the temperature did not exceed 5 °C. The mixture was kept overnight at 5 °C; the precipitate was then filtered off and washed with water. The purification of the raw products was performed by column chromatography (30 × 3 cm SiO_2, CH_2Cl_2) and recrystallization as described below.

(8*E*,17*E*,26*E*)-3,4,5,12,13,14,21,22,23-Nonapropoxytris(1-azaphenanthro[2,1,10-*abc*:2,1,10-*ghi*:2,1,10-*mno*]cyclooctadecene (9a): Yield 0.34 g (30%) of yellow crystals, m.p. >200 °C (decomp). IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1}, 1601, 1483, 1362, 1261, 1088, 734. ^1H NMR ($CDCl_3$): δ = 1.12 (t, 27 H, CH_3), 1.93 (m, 18 H, CH_2), 4.14 (t, 18 H, OCH_2), 7.19 (s, 3 H, 2-H, 11-H, 20-H), 7.56 (d, ^3J = 8.8 Hz, 3 H, 7-H, 16-H, 25-H), 7.69 (d, ^3J = 16.1 Hz, 3 H, 8-H, 17-H, 26-H), 8.44 (s, 3 H, 1-H, 10-H, 19-H), 9.79 (d, ^3J = 16.1 Hz, 3 H, 9-H, 18-H, 27-H), 9.90 (d, ^3J = 8.8 Hz, 3 H, 6-H, 15-H, 24-H). ^{13}C NMR ($CDCl_3$): δ = 10.7 (CH_3), 22.7, 23.7, 26.9 (CH_2), 70.2, 75.2, 75.8 (OCH_2), 106.2 (C-2, C-11, C-20), 118.7, 124.5, 129.1, 133.4 (C-1a, C-10a, C-19a; C-5a, C-14a, C-23a; C-5b, C-14b, C-23b; C-9a, C-18a, C-27a), 122.3 (C-7, C-16, C-25), 125.9, 128.4, 128.9 (C-1, C-10, C-19; C-8, C-17, C-26; C-9, C-18, C-27), 135.1 (C-6, C-15, C-24), 142.6, 146.0, 151.6, 152.7, 152.8 (C-3, C-12, C-21; C-4, C-13, C-22; C-5, C-14, C-23; C-7a, C-16a, C-25a; C-27a, C-28a, C-29a). FD-MS: *m*/*z* (%) = 1132 (100)[26] [$M^{+\cdot}$], 566 (10) [M^{2+}]. $C_{72}H_{81}N_3O_9$ (1132.4): calcd. C 76.36, H 7.21, N 3.71; found C 76.36, H 7.15, N 3.55.

(8*E*,17*E*,26*E*)-3,4,5,12,13,14,21,22,23-Nonadecyloxytris(1-azaphenanthro[2,1,10-*abc*:

2,1,10-*ghi*:2,1,10-*mno*]cyclooctadecene (9b): Yield 605 mg (30%) of a yellow, viscous wax. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 27 H, CH_3), 1.24 (m, 126 H, CH_2), 1.91 (m, 18 H, CH_2), 4.16 (m, 18 H, OCH_2), 7.19 (s, 3 H, 2-H, 1-H, 20-H), 7.57 (d, ^3J = 8.8 Hz, 3 H, 7-H, 16-H, 25-H), 7.71 (d, ^3J = 16.1 Hz, 3 H, 8-H, 17-H, 26-H), 8.46 (s, 3 H, 1-H, 10-H, 19-H), 9.83 (d, ^3J = 16.1 Hz, 3 H, 9-H, 18-H, 27-H), 9.91 (d, ^3J = 8.8 Hz, 3 H, 6-H, 15-H, 24-H). FD-MS: *m*/*z* (%) = 2016 (100)[26] [$M^{+\cdot}$]. $C_{135}H_{207}N_3O_9$ (2016.1): calcd. C 80.43, H 10.35, N 2.08; found C 80.90, H 10.72, N 1.80.

(8*E*,17*E*,26*E*)-3,4,5,12,13,14,21,22,23-Nonadodecyloxytris(1-azaphenanthro[2,1,10-*abc*:2,1,10-*ghi*:2,1,10-*mno*]cyclooctadecene (9c): Preparation as described above; Purification with CH_2Cl_2 on a silica gel column (6 × 8 cm) which contained on the top a layer (2 × 8 cm) of basic Al_2O_3. Yield: 750 mg (33%) of an orange solid, m.p. 19.5 °C (twice recrystallized from acetone/ethyl acetate, 1:1). ^1H NMR ($CDCl_3$): δ = 0.87 (t, 27 H, CH_3), 1.27 (m, 144 H, CH_2), 1.55 (m, 18 H, CH_2), 1.87 (m, 6 H, CH_2), 1.95 (m, 12 H, CH_2), 4.15 (m, 18 H, OCH_2), 7.17 (s, 3 H, 2-H, 11-H, 20-H), 7.56 (d, ^3J = 8.8 Hz, 3 H, 7-H, 16-H, 25-H), 7.69 (d, ^3J = 16.1 Hz, 3 H, 8-H, 17-H, 26-H), 8.44 (s, 3 H, 1-H, 10-H, 19-H), 9.81 (d, ^3J = 16.1 Hz, 3 H, 9-H, 18-H, 27-H), 9.90 (d, ^3J = 8.8 Hz, 3 H, 6-H, 15-H, 24-H). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.3, 29.4, 29.6, 29.7, 30.6, 32.0 (CH_2, partly superimposed), 68.7, 73.8, 74.2 (OCH_2), 106.2 (C-2, C-11, C-20), 118.7, 124.6, 129.1, 133.4 (C-1a, C-10a, C-19a; C-5a, C-14a, C-23a; C-5b, C-14b, C-23b; C-9a, C-18a, C-27a), 122.3 (C-7, C-16, C-25), 125.8, 128.4, 128.9 (C-1, C-10, C-19; C-8, C-17, C-26; C-9, C-18, C-27), 135.1 (C-6, C-15, C-24), 142.7, 146.0, 151.7, 152.8, 152.9 (C-3, C-12, C-21; C-4, C-13, C-22; C-5, C-14, C-23; C-7a, C-16a, C-25a; C-27a, C-28a, C-29a). FD-MS: *m*/*z* (%) = 2268 (100)[26] [$M^{+\cdot}$], 1134 (5) [M^{2+}]. $C_{153}H_{243}N_3O_9$ (2268.6): calcd. C 81.00, H 10.80, N 1.85; found C 80.99, H 10.82, N 1.77.

Although the Schiff bases can be used in situ, one example was isolated and characterized, namely **(*E*)-5,6,7-Tridodecyloxy-2-methylbenzo[*f*]quinoline-10-(*N*-phenyl)carbaldimine (8c):** Aldehyde **7c** (1.33 g, 1.72 mmol) yielded in the procedure described above 1.46 g (100%) of **8c** as a yellow oil. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 9 H, CH_3), 1.25 (m, 48 H, CH_2), 1.53 (m, 6 H, CH_2), 1.87 (m, 6 H, CH_2), 2.74 (s, 3 H, 2-CH_3), 4.11 (m, 6 H, OCH_2), 7.24 (m, 2 H, 8-H and *p*-H of phenyl), 7.36 (d, 2 H, *o*-H of phenyl), 7.39 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.43 (m, 2 H, *m*-H of phenyl), 8.72 (s, 1 H, 9-H), 9.78 (d, ^3J = 8.8 Hz, 1 H, 4-H), 9.93 (s, 1 H, CHN). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.2, 29.2, 29.4, 29.5, 29.5, 29.6, 29.7, 30.5, 31.9 (CH_2, partly superimposed), 24.9 (2-CH_3), 68.7, 73.8, 74.2 (OCH_2), 107.2 (C-8), 120.0, 123.3, 128.4, 130.4 (C-4a, C-4b, C-8a, C-10), 121.4 (*o*-C, phenyl), 121.6 (C-3), 125.7 (*p*-C, phenyl), 129.1 (*m*-C, phenyl), 129.2 (C-9), 135.0 (C-4), 143.7, 145.7, 151.5, 152.8, 153.0 (C-5, C-6, C-7, C-10a, *i*-C of phenyl), 156.3 (C-2), 159.6 (CHN). FD-MS: *m*/*z* (%) = 849 (100) [$M^{+\cdot}$]. $C_{57}H_{88}N_2O_3$ (849.3): calcd. C 80.61, H 10.44, N 3.30; found C 80.56, H 10.51, N 3.36.

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