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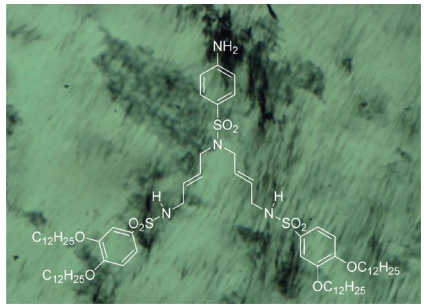
Liquid Crystals

Polar groups play an important role in the organization of arylsulfonamide derivatives in mesophases. Hydrogen-bonding interactions between amino groups or dipole···dipole interactions between CF or CN groups are responsible for the forces that characterize the cohesion of molecules in hexagonal columnar mesophases.



Keywords: Liquid crystals / Hydrogen bonds / Electrostatic interactions / Sulfonamides / Macrocycles

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Polar Groups and Arylsulfonamides: A Good Combination with which to Obtain Supramolecular Columnar Liquid Crystals

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Keywords: Liquid crystals / Hydrogen bonds / Electrostatic interactions / Sulfonamides / Macrocycles

Mesomorphic arylsulfonamide derivatives containing four long alkyl chains and polar groups (fluoro, cyano or amino) have been synthesized and characterized by polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction on the mesophase. Studies of the supramolecular organization of these molecules have allowed a better understanding of the noncovalent driving forces (dipole···dipole and hydrogen-bonding interactions) responsible for the self-assembly, which is mainly due to the presence of the polar groups.

Introduction

Noncovalent intermolecular interactions are mainly responsible for the spontaneous self-assembly of simple molecules in liquid crystalline materials. Hydrogen-bonding, dipole···dipole, ionic, π-π stacking, and van der Waals forces are the most commonly used interactions in the preparation of these materials with organization-dependent properties.[1–4]

Columnar liquid crystals (LC) are well-known examples of supramolecular assemblies and have received considerable interest as functional materials for applications in organic electronics and optoelectronics.[5–7] Hydrogen-bonding has been used to organize discotic molecules[8,9] or to arrange complementary precursors to form discs that can be self-assembled into columns.[10,11] Dipole···dipole interactions between polar groups have also been used in the latter approach.[12] For example, bent-core mesogens with cyano groups can be used to achieve columnar organizations with a macroscopic dipole along the column,[13] which may show ferroelectric switching.[13b,13c] Likewise, the influence of a fluoro substituent in LC molecules has also been studied, mainly because of its small size, high electronegativity, and large C–F bond-dissociation energy. Intermolecular dipole···dipole interactions between C–F bonds have been employed to influence the mesomorphism of calamitic mesogens,[14] or bent-core mesogens;[15] however, this effect has rarely been studied for the generation of columnar mesophases.[16]

We previously reported that several 15-membered triolefinic azamacrocycles prepared from arylsulfonamides containing long hydrocarbon or polyfluorinated chains and their open chain precursors showed liquid crystalline properties.[11] The rigidity of backbones in macrocyclic molecules, together with the presence of long tails and the existence of terminal sulfonamides ($NHSO_2R$) in open precursors, favored the organization of molecules in mesophases. The aim of the present work was to analyze how the presence of polar functional groups, such as fluoro, cyano, and amino, could affect the organization of this type of molecule and the generation of liquid crystalline behavior. Accordingly, we designed new macrocycles that contain a total of four alkoxy tails linked to two of the aromatic rings (two chains per ring), and a polar group such as a fluoro (**6a** and **7a**), a cyano (**6b** and **7b**), or amino (**6c** and **7c**) in the *para* position of the third aromatic ring. For comparative purposes, this series was completed with the corresponding compounds bearing a hydrogen atom instead of polar groups (**6d** and **7d**). The new macrocycles and their open precursors were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction techniques. The presence of intermolecular interactions (mainly hydrogen bonds or dipole···dipole interactions) was considered in order to develop models for the molecular organization in the mesophases.

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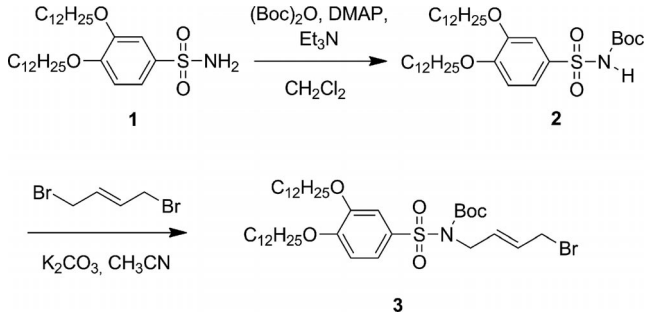
Results and Discussion

Synthesis

The Boc-protected derivative (**2**) of 3,4-bis(dodecyloxy)-benzenesulfonamide (**1**) was used to prepare the alkylated compound **3** as described previously (Scheme 1).[11a] The combination in a basic medium of two molecules of **3** with one molecule of four different arylsulfonamides, substituted in the *para* position with fluoro, cyano and amino groups (**4a**–**c**, respectively, Scheme 2) and the nonsubstituted derivative **4d** allowed the preparation of trisulfonamides **5a**–**d**, which were subsequently deprotected in an acidic medium (trifluoroacetic acid/CH_2Cl_2, 1:1) to give the corresponding open precursors **6a**–**d** in good to excellent yields (61–99%).



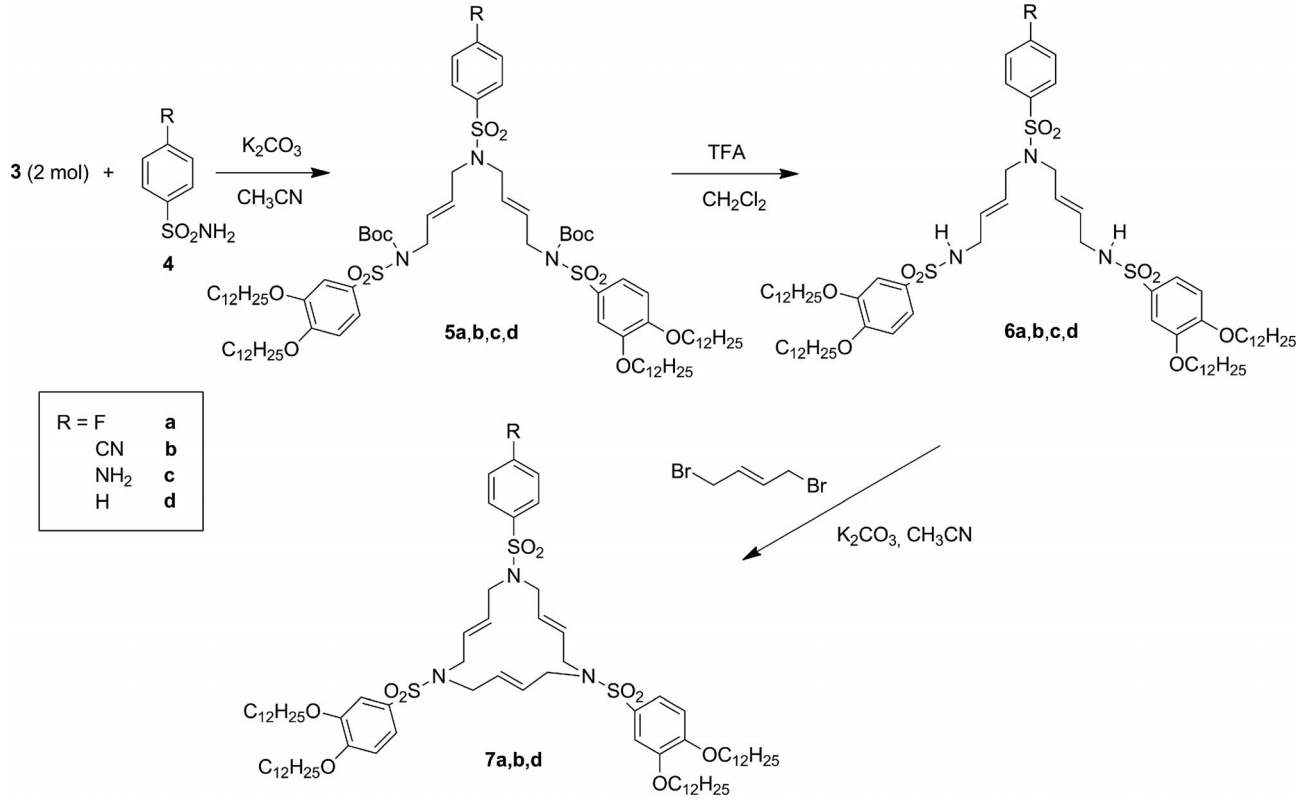
Scheme 1. Synthesis of macrocyclic precursors derived from arylsulfonamide **1**.

Macrocycles **7a**, **7b**, and **7d** were obtained by cyclization of compounds **6a**, **6b**, and **6d**, respectively, with (*E*)-1,4-dibromo-2-butene, using potassium carbonate base in anhydrous acetonitrile (Scheme 2). The same reaction on **6c** was unsuccessful; in this case a complex reaction mixture was obtained, probably due to competition in the reaction between sulfonamido and amino groups. Another strategy was therefore used for the synthesis of **7c**[17] that involved the introduction of sulfonamide **4c** in the last step. This procedure was used to obtain **7c** in good yield from dibromoderivative **9** (Scheme 3).

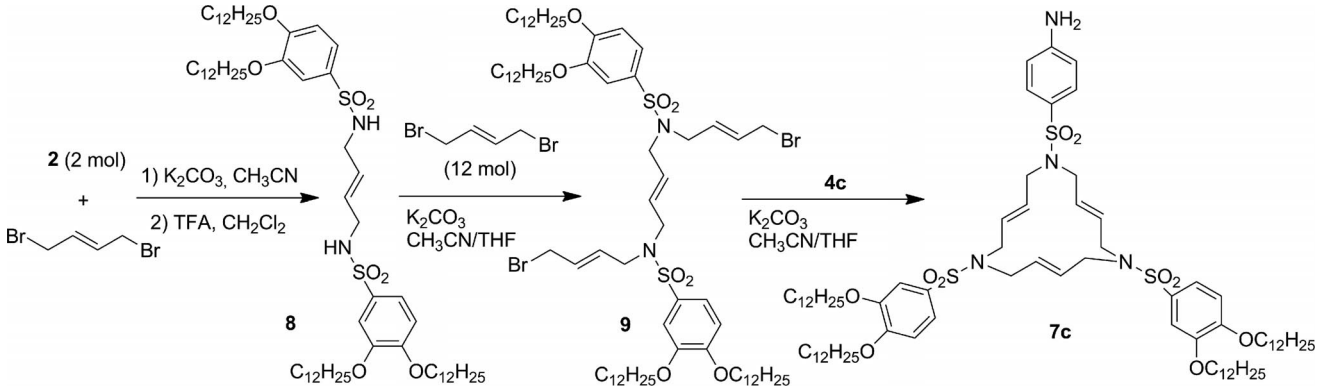
Mesomorphic Behavior

The thermal behavior of compounds **6a**–**d** and **7a**–**d** was studied by POM and DSC; the results are gathered in Table 1.

The open precursors **6a** and **6b** showed monotropic mesomorphic behavior and displayed poorly defined textures by POM that are indicative of Col_h mesophases. The stability of the mesophase of **6a** was very low and it was seen too be under kinetic control upon cooling the isotropic liquid at a rate of 20 °C/min (Figure 1, a). When cooling at 10 °C/min, the mesophase coexisted with the crystalline phase (Table 1), and at 5 °C/min no mesomorphic behavior but crystallization was observed (see the Supporting Information). For **6b**, the mesophase was only observed on cooling from the isotropic liquid (Figure 1, b). In contrast, the



Scheme 2. Synthesis of open precursors **5** and **6** and macrocycles **7a**, **7b**, and **7d**.



Scheme 3. Synthesis of macrocycle **7c**.

Table 1. Thermal and thermodynamic properties calculated during the second heating-cooling cycle (DSC experiments recorded at 10 °C/min). Temperatures are given in °C. Enthalpies are given in kJ mol^{-1} and appear in parentheses.

	Thermal and thermodynamic properties
6a[a]	C 94.5 (83.0) I I 67.2 (1.9) Cr + I 57.8 (2.0) Cr + Col_h [b] 37.6 (30.6) Cr
6b[a]	Cr 98.0 (57.1) I I 79.3 (2.4) Col_h 49.2 (32.6) Cr
6c	Cr 40.2 (28.7) Col_h 92.6 (1.3) I I 90.3 (1.2) Col_h 31.2 (21.0) Cr
6d	Cr 40.4 (31.8) Col_h 45[c] I I 42.2 (1.5) Col_h 31.0 (23.9) Cr
7a	Cr 40.0[d] (7.6) Col_h 60.4 (4.3) I I 59.2 (5.0) Col_h 34.0[d] (8.5) Cr
7b	Cr 55.4[d] (8.2) Col_h 83.2 (4.1) I I 82.5 (5.3) Col_h 49.2[c] (5.9) Cr
7c	Cr 56[e] I
7d	Col_{h1} 30.4 (5.9) Col_{h2} 47.9 (2.0) I 53.3 (–34.8)[f] Cr 77.2 (34.2) I I 45.7 (4.1) Col_{h2} 35.8 (3.9) Col_{h1}

[a] Monotropic behavior. [b] Crystal phase coexisted with isotropic liquid or mesophase (see the Supporting Information). [c] Shoulder of the peak corresponding to melting. [d] Temperatures taken at the maximum of the broad peaks. [e] Temperature taken by POM. [f] Cold crystallization.

amino derivative **6c** showed an enantiotropic mesophase over a broad temperature range. The focal-conic texture of this mesophase, which appeared on cooling the isotropic state (Figure 1, c), is consistent with a hexagonal columnar organization.

For open precursors **6a**–**c** it is envisaged that competition between different types of noncovalent interactions leads to the different thermal behavior. Thus, for fluoro and cyano derivatives **6a** and **6b**, respectively, strong dipole···dipole interactions must compete with the possibility of H-bonding interactions between sulfonamide groups[11a] and with the subtle forces responsible for mesomorphic arrangements, and therefore crystal structures are produced rather than stable fluid mesophases. This is not the case for compound **6c**, which has a much lower melting temperature than **6a** and **6b**. This compound has the possibility of forming intermolecular hydrogen bonds promoted by amino groups and these could account for the stability of the mesophase. In terms of explaining the formation of a stable mesophase,

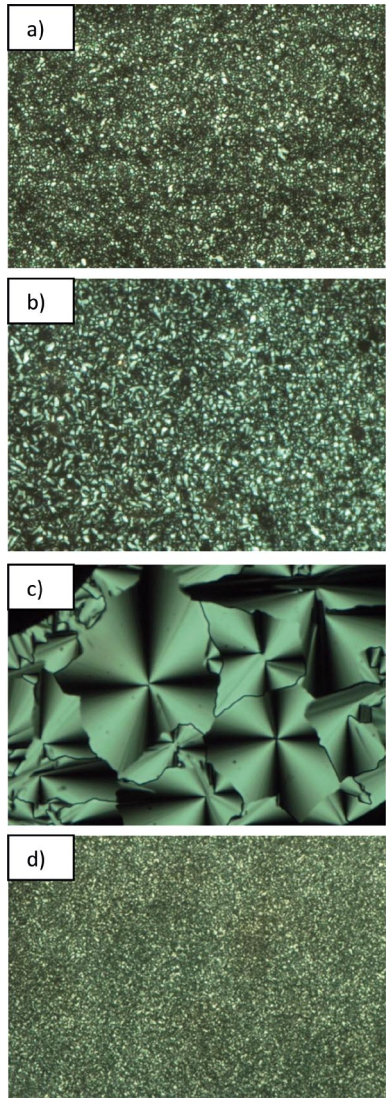


Figure 1. (a) Texture of the mesophase observed for **6a**, at 55 °C, at a cooling rate of 20 °C/min from the isotropic liquid (×20). (b) Texture of the Col_h mesophase observed for **6b**, at 73 °C (×20). (c) Focal conic texture observed for **6c**, at 97 °C (×20). (d) Texture of the Col_h mesophase observed for **6d**, at 38 °C, on cooling (×20).

and later supported by X-ray diffraction, intermolecular H-bonds between sulfonamide groups can be ruled out be-

cause the final supramolecular structure would require a disposition of flexible tails that is not favorable for mesophase formation. Compound **6d** showed undefined textures through the POM, reminiscent of Col_h mesomorphism. For the stability of this mesophase, it can be deduced that intermolecular interactions are less favored given the lower melting and clearing temperatures, compared to **6a**–**c**. Even though the mesophase is enantiotropic according to the thermogram recorded at 10 °C/min (see the Supporting Information), the mesomorphic range is very short, especially compared with cyano and amino derivatives.

Macrocycles **7a** and **7b** showed stable mesophases with hexagonal columnar organizations identified by their textures by POM (Figure 2, a and b). In contrast, compound **7c** did not present mesomorphic behavior. Unsubstituted compound **7d** showed a rather complex thermal behavior with metastable Col_h mesomorphism, which undergoes cold crystallization on heating. On cooling, the thermogram presented two peaks. The first, at 45.7 °C, is associated with the transition between the isotropic liquid and a Col_h mesophase, which showed a poorly defined texture. A second exothermic peak was visible at 30.4 °C, which should correspond to a thermal transition to a second mesophase that, however, did not show clear texture differences (Figure 2, c).

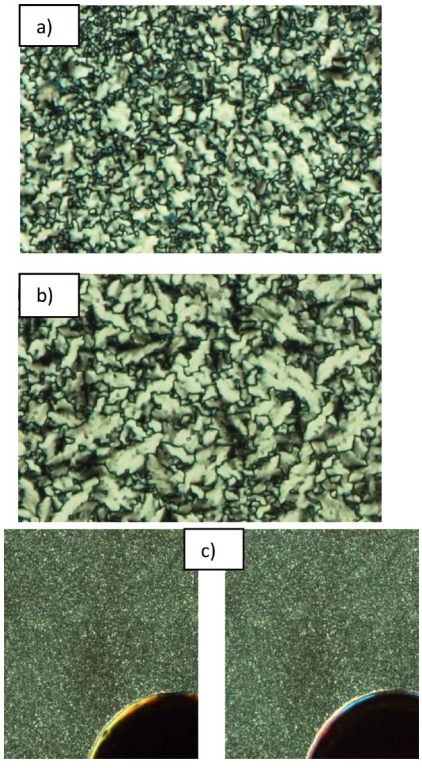


Figure 2. Photomicrographs of the textures observed by polarizing optical microscopy on cooling from the isotropic state: (a) Compound **7a** Col_h mesophase at 53.1 °C (×20); (b) Compound **7b** Col_h mesophase at 70.0 °C (×20). (c) Texture of the Col_{h1} mesophase observed for **6d** at 28 °C (left) and of the Col_{h2} at 38 °C (right) (×20).

In comparison to the corresponding open precursors **6a** and **6b**, melting temperatures decrease significantly for fluoro (**7a**) and cyano (**7b**) derivatives, respectively. It can be deduced that dipole···dipole interactions must not be strong enough to favor crystalline behavior as observed for **6a** and **6b**, and a stable mesomorphic state is observed. Furthermore, when compared with previously described azamacrocyclic structures that contain two long alkoxy tails in each aromatic ring,[11a] it is significant that the latter showed shorter mesomorphic temperature ranges than **7a** and **7b** (45.3–46.7 °C and 20–30 °C, respectively), while maintaining the same type of mesophase. This fact leads one to consider dipole···dipole interactions as a crucial factor that favors mesomorphic properties in these molecules, and this will affect the models proposed for the organization of molecules in the mesophase (see below). Furthermore, when compared with the unsubstituted macrocycle **7d**, it can be deduced that the presence of polar groups clearly stabilizes the Col_h mesomorphism, likely due to dipole···dipole interactions. Once again, these results are in contrast to those found for the amino derivative **7c**, which did not show mesomorphic behavior. The melting temperature of **7c** is similar to that of **7b**, which means that the difference is not a matter of stabilization of the crystalline state but that the mesomorphic behavior in this case is not favored on increasing the rigidity of the constituent molecules by cyclization. The variable influence of dipole···dipole and H-bonding interactions on mesomorphism is related to the presence or absence of the macrocyclic ring and this confirms that mesomorphism is the result of a subtle balance of intermolecular forces.

X-ray Diffraction

X-ray diffraction studies were performed on the liquid crystal phases of the five mesogenic compounds that showed enantiotropic mesophases (compounds **6c**, **6d**, **7a**, **7b**, and **7d**; Table 2). The monotropic character of mesophases of **6a** and **6b** precluded their characterization by X-ray diffraction. They crystallized during the X-ray experiments because their isotropic-mesophase transition temperature is well below their melting point.

The X-ray patterns confirm that the mesophase of **6c** is unambiguously Col_h. A sharp, strong maximum at 38.9 Å and two reflections of medium intensity at 22.8 and 19.3 Å in the small-angle region were observed. These results correspond to a reciprocal spacing ratio $1:3^{1/2}:2$, associated, respectively, to the (10), (11), and (20) reflections of a two-dimensional hexagonal liquid crystalline lattice, with a lattice constant a of 45 Å (Table 2). This constant is larger than the value obtained for the similar derivative containing two long hydrocarbon chains in the aromatic ring instead of the amino compound (35.6 Å),[11a] despite the smaller size of the molecule. From the measured lattice constant, the column cross section can be calculated as $S = a^2\sqrt{3}/2$, with a value of 1775 Å^2 obtained for **6c**. This value is too high for stacking of single molecules and is consistent with

Table 2. Structural data for the mesophases measured by X-ray diffraction.[a]

	T [°C]	Mesophase	Parameters [Å]	d_{exp}[b]	d_{cal}	Z[d]
6c	70	Col_h	a = 45.0	38.9	39.0	3
				22.8	22.5	
				19.3	19.5	
				4.5 *diff*		
6d	44	Col_h	a = 40.6	35.2	35.2	2–3
				4.5 *diff*		
7a	60	Col_h	a = 38.4	33.3	33.3	2
				4.7 *diff*		
7b	70	Col_h	a = 43.2	37.4	37.4	3
				4.7 *diff*		
7d	t.a.	Col_{h1}	a = 45.4	39.3	39.3	3
				4.4[c]		
	41	Col_{h2}	a = 41.2	35.7	35.7	2–3

[a] The columns list, respectively, the compound number, the temperature of the experiment, the mesophase type, the measured parameters (a: lattice constant in the columnar mesophase), the experimentally-measured spacing, the calculated spacing, and the estimated number of molecules per lattice. [b] *diff* signifies diffuse. [c] Relatively narrow, strong halo. [d] See text.

the existence of aggregates in which hydrogen-bonding interactions between amino groups in the center of the column and external van der Waals interactions between long chains favor stack formation (Figure 3, a).

When macrocycles **7a** and **7b** were studied by X-ray diffraction, only one small-angle maximum was observed and this can be assigned to the (10) reflection of a hexagonal columnar (Col_h) mesophase. The deduced hexagonal lattice constants a are 38.4 and 43.2 Å, respectively (Table 2). The difference of around 5 Å shows that the organization of the molecules in the mesophases should be drastically different; replacement of a fluoro-substituent by a cyano group should not produce such a change if only steric effects are considered (volume change). Calculated cross sections are 1279 Å for **7a** and 1616 Å for **7b**. Once more, these values are too large for stacking of single molecules. It can be predicted on the basis of density estimations that each disc of the columns should be composed of several molecules, as shown in Figure 3 (b and c). This kind of structure is in reasonable agreement with other similar structures proposed by us.[11] The aggregation phenomenon must be due to the dipole···dipole interactions between C–F bonds and C≡N groups, respectively.

The number (Z) of molecules per disc (column stratum) can be estimated on the basis of the expected density for typical organic compounds. The density ρ in $g\,cm^{-3}$ of a columnar mesophase can be calculated using the equation:

$$\rho = (M \cdot Z \cdot 10^{24})/(V \cdot N_A)$$

where M is the molar mass in g, V the unit cell volume in $Å^3$ and N_A Avogadro's number. Assuming that the density of the organic compounds is close to 1 $g\,cm^{-3}$ and taking into account that the volume of the unit cell is $S \cdot c$, where S and c are the cross-sectional area and the height of the cell, respectively, Z can be estimated as:

$$Z = (S \cdot c \cdot N_A)/(M \cdot 10^{24})$$

In this equation, c (height of the unit cell or thickness of a column stratum) is unknown because of the absence of a

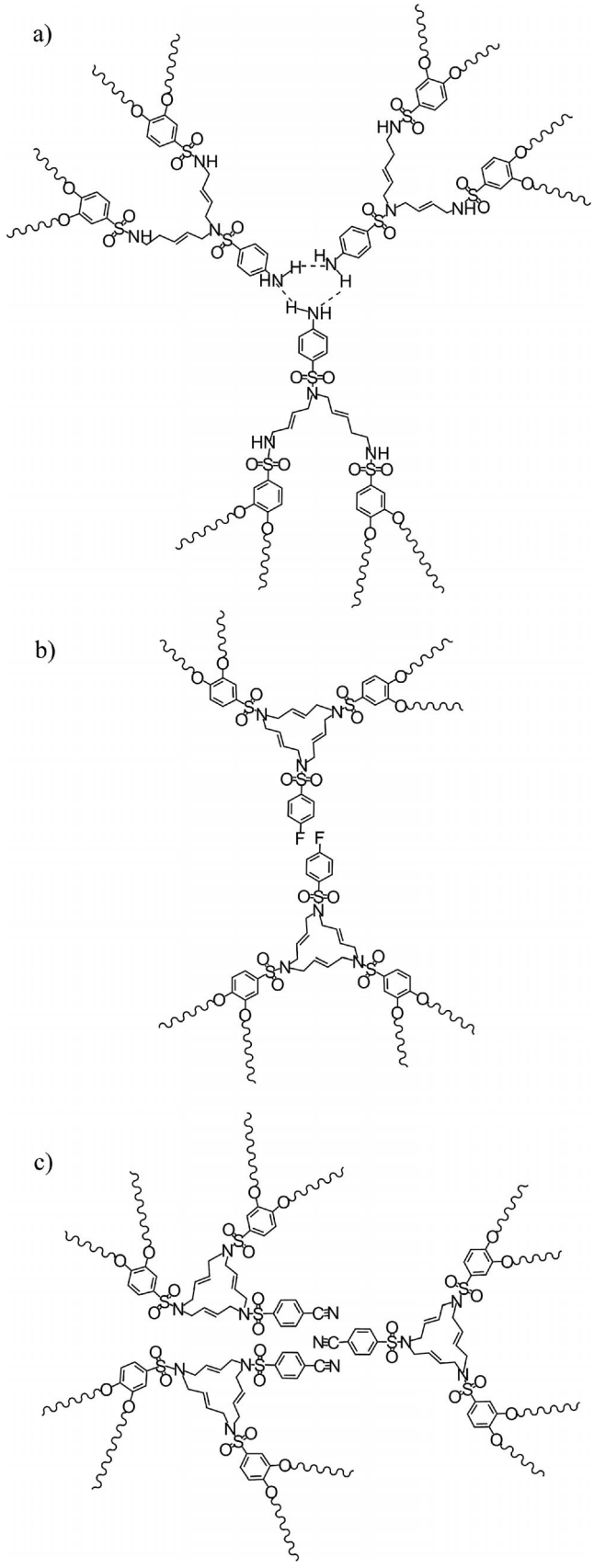


Figure 3. Simplified models for (a) **6c**, (b) **7a**, and (c) **7b** showing hydrogen bond interactions or dipole···dipole interactions.

scattering maximum due to the stacking distance as a consequence of the lack of long-range periodicity along the column axis. However, it is reasonable to consider that a rough value can be deduced from the diffuse halo recorded at high angles in the scattering patterns (see Table 2). On the basis of these assumptions it is estimated that about three molecules (Z = 3) of compound **6c**, two molecules (Z = 2) of **7a**, and three molecules (Z = 3) of **7b** are needed on average to fill a column stratum with a thickness of about 4–4.5 Å (see Figure 3). The stratum thickness would increase to about 4.5–5 Å considering a density of 0.9 $g cm^{-3}$. In all cases, the outside of the columns should be coated with a large number of hydrocarbon chains (eight or twelve for *Z* values of two or three, respectively), as usually found in classical columnar mesophases generated by single disc-shaped molecules.

The dipole···dipole interactions between the C–F or C≡N groups take place by antiparallel arrangement of these groups. Indeed, in the case of **7b**, there is a two-by-two association of molecules with an antiparallel orientation of their C–F dipoles to maximize the electrostatic interactions (Figure 3, b). For **7c**, a similar kind of antiparallel arrangement occurs, but X-ray results suggest that, in this case, the molecules associate in groups of three, preserving the antiparallel orientation of the polar groups (Figure 3, c).

X-ray diffractograms of the nonsubstituted analogues **6d** and **7d** were difficult to obtain due to the narrow thermal range of their mesophases and the tendency for cold crystallization of **7d**. For this reason, only short-exposure-time patterns were recorded. Only one small-angle reflection was obtained and this can be assigned to the (10) reflection of a hexagonal columnar (Col_h) mesophase. The two mesophases exhibited by **7d** yielded similar patterns, except for the narrower and stronger character of the large-angle halo for the lower-temperature phase. This denotes that this phase is more ordered than the higher-temperature mesophase, for which this scattering halo is practically not observed. Furthermore, the hexagonal lattice constant *a* changes noticeably, probably due to a different kind of intermolecular association. The estimated *Z* values for **6d** and **7d** are between two and three (Table 2), although this association must be weaker than for compounds bearing polar groups.

The absence of (11) and (20) reflections in the X-ray patterns of **6d**, **7a**, **7b**, and **7d** is related to the low electron density of the central core of the supramolecular disc. This produces a poor contrast in the electron density function and therefore the intensity of the peaks is reduced as their angle increases. In addition, the structure is smeared out compared with the amino-substituted analogue due to the weaker character of the dipolar forces or van der Waals interactions compared with hydrogen-bonding.[18]

It must be pointed out that the structures proposed are idealized models. Due to the fluid nature of the mesophases, the molecule positions fluctuate, so intermolecular association do not need to be within the same plane (supramolecular disc) but can also arise between adjacent planes along the column. In fact, it is not possible for the mutually-associated molecules to be in the same plane because they depart from planarity at the nitrogen atoms. Therefore, the estimated *Z* values have to be considered an approximation and, furthermore, they do not need to be integer numbers. However, it can be safely concluded that, depending of the estimated *Z* value, the cross-section of the columns is consistent with the presence in each case of a larger or smaller number of molecules filling the column section.

Conclusions

New liquid crystalline molecules have been obtained by combining two molecules of an arylsulfonamide that bear two long hydrocarbon chains linked to each aromatic ring and a second containing a polar group in the *para* position (fluoro, cyano or amino group). These polar groups play an important role in the organization of molecules in the mesophases; hydrogen-bonding interactions between amino groups or dipole···dipole interactions between C–F or –CN groups are responsible for the forces that characterize the cohesion of molecules in hexagonal columnar mesophases. Indeed, the stability of the columnar mesophases is much higher than that observed for the corresponding compounds devoid of polar groups. The presence of long alkyl chains coating the outside of columns should also be considered, because they are fluid and disordered, allowing the highly dynamic nature of columnar phases.

In cyclic derivatives **7a** and **7c**, the presence of these interactions produces a clear increase in the mesomorphic thermal range, in comparison with similar macrocycles that contain only long alkyl chains. A favorable or unfavorable balance between the different types of interactions (hydrogen bonding between terminal sulfonamides and dipole···dipole interactions) could account for the monotropic behavior found for open precursors **6a** and **6b** and the nonmesomorphic behavior of macrocycle **7c**. It was observed that the variation of the molecular architecture allows control of thermotropic properties and the design of discotic mesophases. Studies of the supramolecular organization of these molecules have provided a better understanding of the noncovalent driving force responsible for their self-assembly. Thus, it has been shown that the columns are formed by supramolecular aggregates that are formed through dipole···dipole interactions (fluoro and cyano derivatives) or H-bonding interactions (amino derivatives).

Experimental Section

General: Melting points were determined with a Kofler apparatus. IR spectra were recorded in attenuated total reflectance mode (ATR) with a Bruker Tensor 27 spectrophotometer. NMR spectra were recorded with Bruker ARX200, DPX250, DPX360 or Bruker AV400 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to tetramethylsilane; coupling constants are reported in Hz. The assignments of ^1H and ^{13}C NMR spectra were carried out using DEPT, NOE, COSY, HMQC, HMBC, and TOCSY experiments when necessary. High-resolution MALDI-

TOF spectra were obtained with a Bruker spectrometer, model BIFLEX (Bruker-Franzen Analityk) with a Modus Reflecton. The ionization was achieved by using a laser source (337 nm with a voltage of 19 kV). Several matrixes were used and details are given in the experimental part for each compound. High-resolution mass spectrometry with electrospray ionization (HRMS-ESI) was performed with a Bruker MicroTOF-Q, using sodium formiate as external reference.

Thermal Properties and Liquid Crystalline Behavior: Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with DSC-MDSC TA instruments Q-1000 and Q-2000; and TA Q-5000, respectively. Liquid crystal textures were studied with an Olympus BX-50 polarizing microscope equipped with a Linkam TMS91 hot-stage and a CS196 hot-stage central processor. Microphotographs were taken with an Olympus DP12–2 digital camera.

Mesophase Structure: XRD measurements were carried out at room temperature with a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-K_α beam. The sample was held in Lindemann glass capillaries (1 mm diameter) perfectly sealed and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on a flat photographic film held perpendicular to the X-ray beam.

Synthesis of Precursors: Compounds **1**–**3** were prepared as reported previously.[10a] Sulfonamides **4a**–**d** were commercially available (Sigma–Aldrich).

Synthesis of Protected Derivatives 5: Sulfonamides **5b**–**d** were obtained by following the same experimental procedure described for **5a** (Scheme 2).

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-6-[(4-fluorophenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (5a): Sulfonamide **2** (2.30 g, 3.1 mmol) was dissolved in anhydrous CH_3CN (85 mL) by heating, and **4a** (0.23 g. 1.3 mmol) and K_2CO_3 (1.1 g, 8.0 mmol) were added. The mixture was heated to reflux for 24 h. Salts were filtered off, washed with hot CH_3CN, and the filtrates were evaporated. The residue was purified by column chromatography (hexane/EtOAc, 9:1). Compound **5a** (1.83 g, 90%) was isolated as an oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.80 (dd, J = 8.9, $J_{H,F}$ = 5.0 Hz, 2 H), 7.42 (dd, J = 8.6, J_{H-F} = 2.2 Hz, 2 H), 6.91 (d, J = 8.6 Hz, 2 H), 5.73 (m, 2 H), 5.51 (m, 2 H), 4.34 (d, J = 5.4 Hz, 4 H), 4.02 (dt, J = 10.2, 6.6 Hz, 8 H), 3.84 (d, J = 6.2 Hz, 4 H), 1.82 (m, 8 H), 1.33 (s, 18 H), 1.43 (m, 8 H), 1.25 (complex signal group, 64 H), 0.87 (t, J = 6.8 Hz, 12 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 163.6 (d, $J_{C,F}$ = 254.1 Hz), 153.3, 150.7, 148.4, 136.4 (d, $J_{C,F}$ = 3.3 Hz), 131.3, 130.6, 129.8 (d, $J_{C,F}$ = 9.3 Hz), 127.3, 121.9, 116.3 (d, $J_{C,F}$ = 22.6 Hz), 112.7, 111.7, 84.2, 69.6, 69.2, 47.8, 47.7, 31.9, 29.7, 29.8, 29.6, 29.4, 29.1, 29.0, 27.9, 26.0, 25.9, 22.7, 14.1 ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = 105.7 ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2852, 1728, 1589, 1508, 1355, 1263, 1140 cm^{-1}. MS (ESI): m/z calcd. for $C_{84}H_{140}FN_3O_{14}S_3$ $[M]^+$ 1529.86; found 685.0 $\{M[-OC(CH_3)_3] + Ca\}^{2+}$. $C_{84}H_{140}FN_3O_{14}S_3$ (1531.22): calcd. C 65.90, H 9.20, N 2.74; found C 66.30, H 9.53, N 3.14.

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-6-[(4-cyanophenyl)sulfonyl]-1,11-bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene (5b): Isolated yield: 0.40 g (65%); oil at room temperature. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.5 Hz, 2 H), 7.82 (d, J = 8.5 Hz, 2 H), 7.42 (dd, J = 8.5, 2.1 Hz, 2 H), 7.35 (d, J = 2.1 Hz, 2 H), 6.91 (d, J = 8.5 Hz, 2 H), 5.79 (m, 2 H), 5.53 (m, 2 H), 4.35 (d, J = 5.1 Hz, 4 H), 4.03 (app. q, J = 6.6 Hz, 8 H), 3.89 (d, J = 6.2 Hz, 4 H), 1.86–1.68 (m, 8 H), 1.34 (s, 18 H), 1.54–1.24 (complex signal group, 72 H), 0.87 (t, J = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 153.6, 150.9, 148.8, 133.3, 131.6, 131.4, 127.9, 126.7, 122.0, 113.2, 112.1, 84.4, 69.9, 69.5, 48.0, 47.8, 32.1, 29.8, 29.5, 29.3, 29.2, 28.1, 26.1, 22.8, 14.2 ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2852, 2232, 1726, 1508, 1353, 1137, 922, 719, 626 cm^{-1}. MALDI-TOF MS (Ditranol): m/z calcd. for $C_{85}H_{140}N_4O_{14}S_3$ $[M]^+$ 1536.9; found 1575.8 $[M + K]^+$. $C_{85}H_{140}N_4O_{14}S_3$ (1537.23): calcd. C 66.37, H 9.17, N 3.64; found C 66.64, H; 9.42, H 3.95.

(*E*,*E*)-6-[(4-Aminophenyl)sulfonyl]-1,11-bis(*tert*-butyloxycarbonyl)-1,11-bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene (5c): Isolated yield: 0.50 g (75%); oil at room temperature. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 2.2 Hz, 2 H), 7.43 (dd, J = 8.3, 2.2 Hz, 2 H), 6.92 (d, J = 8.3 Hz, 2 H), 6.68 (d, J = 8.8 Hz, 2 H), 5.72 (m, 2 H), 5.63 (m, 2 H), 4.23 (d, J = 6.2 Hz, 4 H), 4.08 (br. s, 2 H, NH), 4.02 (m, 8 H), 3.78 (d, J = 6.2 Hz, 4 H), 1.82 (m, 8 H), 1.38 (s, 18 H), 1.54–1.26 (complex signal group, 72 H), 0.87 (t, J = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 153.6, 150.9, 148.7, 131.5, 130.2, 129.2, 128.0, 126.3, 122.1, 113.1, 112.1, 84.3, 69.9, 69.4, 48.0, 32.1, 29.8, 29.5, 29.2, 28.1, 26.1, 22.8, 14.2 ppm. IR (ATR): $\tilde{\nu}$ = 3478, 3380, 2921, 2852, 1726, 1506, 1351, 1137, 918, 719, 626 cm^{-1}. MALDI-TOF MS (dithranol): m/z calcd. for $C_{84}H_{142}N_4O_{14}S_3$ $[M]^+$ 1526.8; found 1565.8 $[M + K]^+$. $C_{84}H_{142}N_4O_{14}S_3$ (1528.24): calcd. C 66.02, H 9.37, N 3.67; found C 66.40, H 9.61, N 3.99.

(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-6-(phenylsulfonyl)-1,6,11-triazaundeca-3,8-diene (5d): Compound purified by column chromatography (hexane/EtOAc, 8:2). Isolated yield: 1.20 g (81%); oil at room temperature. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.1 Hz, 2 H), 7.55 (m, 3 H), 7.44 (dd, J = 8.6, 2.0 Hz, 2 H), 7.38 (d, J = 2.0 Hz, 2 H), 6.93 (d, J = 8.6 Hz, 2 H), 5.76 (m, 2 H), 5.57 (m, 2 H), 4.35 (d, J = 5.4 Hz, 4 H), 4.03 (dt, J = 10.6, 6.5 Hz, 8 H), 3.85 (d, J = 6.2 Hz, 4 H), 1.90–1.80 (m, 8 H), 1.47 (m, 8 H), 1.35 (s, 18 H), 1.27 (br. s, 64 H), 0.89 (t, J = 6.7 Hz, 12 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 153.2, 150.7, 148.4, 140.2, 132.6, 131.2, 130.3, 129.2, 127.8, 127.1, 121.9, 121.8, 112.8, 112.7, 111.8, 84.2, 69.6, 69.2, 48.1, 47.7, 31.9, 29.7, 29.6, 29.4, 29.1, 29.0, 28.2, 27.9, 27.7, 26.0, 22.7, 14.1 ppm. IR (ATR): $\tilde{\nu}$ = 2923, 2853, 1727, 1587, 1509, 1468, 1355, 1262, 1158, 1140 cm^{-1}. MALDI-TOF MS (dithranol/NaTFA): m/z calcd. for $C_{84}H_{141}N_3O_{14}S_3$ $[M]^+$ 1511.96; found 1334.9 $\{M[-OC(CH_3)_3] + Na\}^+$. $C_{84}H_{141}N_3O_{14}S_3$ (1513.23): calcd. C 66.67, H 9.39, N 2.78; found C 66.50, H 9.55, N 2.89.

Synthesis of Open Precursors 6: Compounds **6b**–**d** were obtained by following the same experimental procedure described for **6a** (Scheme 2).

(*E*,*E*)-1,11-Bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-6-[(4-fluorophenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (6a): Compound **5a** (1.2 g, 0.81 mmol) was dissolved in CH_2Cl_2 (15 mL). Trifluoroacetic acid (TFA; 15 mL) was added and the mixture was stirred for 4 h at room temperature. The solvent and excess of acid were evaporated and the residue was dissolved in CH_2Cl_2 and extracted three times with water. The organic phase was dried with anhydrous Na_2SO_4, filtered, and the filtrate was evaporated. The residue was purified by flash column chromatography to give **6a**, yield 0.65 g (61%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.79 (dd, J = 8.5, $J_{H,F}$ = 5.0 Hz, 2 H), 7.42 (dd, J = 8.5, $J_{H,F}$ = 2.0 Hz, 2 H), 7.33 (d, J = 2.0 Hz, 2 H), 7.19 (t, J = 8.5 Hz, 2 H), 6.89 (d, J = 8.5 Hz, 2 H), 5.56 (m, 4 H), 5.07 (t, J = 6.3 Hz, 2NH), 4.02 (t, J = 6.5 Hz, 4 H), 3.96 (t, J = 6.5 Hz, 4 H), 3.70 (d, J = 5.4 Hz, 4 H), 3.47 (t, J = 5.4 Hz, 4 H), 1.79 (m, 8 H), 1.43 (m, 8 H), 1.26 (complex signal group, 64 H), 0.88 (t, J = 6.7 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 163.7 (d, $J_{C,F}$ = 254.9 Hz), 152.8, 149.2, 135.9 (d, $J_{C,F}$

= 3.3 Hz), 131.0, 129.9 (d, $J_{C,F}$ = 9.3 Hz), 127.9, 120.9, 116.4 (d, $J_{C,F}$ = 22.5 Hz), 112.2, 111.4, 69.6, 69.3, 49.2, 44.4, 32.0, 29.8, 29.77, 29.5, 29.2, 29.1, 26.1, 22.8, 14.2 ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = 105.6 ppm. IR (ATR): $\tilde{\nu}$ =3313, 2918, 2850, 1589, 1508, 1323, 1259, 1140, 1091, 833 cm^{-1}. HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{74}H_{124}FNaN_3O_{10}S_3$ [M + Na]$^+$ 1352.8325; found 1352.8310.

(*E*,*E*)-6-[(4-Cyanophenyl)sulfonyl]-1,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene (6b): Isolated yield: 0.19 g (99%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.6 Hz, 2 H), 7.83 (d, *J* = 8.6 Hz, 2 H), 7.42 (dd, *J* = 8.6, 2.2 Hz, 2 H), 7.33 (d, *J* = 2.2 Hz, 2 H), 6.90 (d, *J* = 8.6 Hz, 2 H), 5.61 (app. q, *J* = 4.9 Hz, 4 H), 4.96 (t, *J* = 6.3 Hz, 2 H, NH), 4.03 (t, *J* = 6.8 Hz, 4 H), 3.98 (t, *J* = 6.8 Hz, 4 H), 3.76 (m, 4 H), 3.49 (app. t, *J* = 5.1 Hz, 4 H), 1.96–1.73 (complex signal group, 8 H), 1.48–1.28 (complex signal group, 72 H), 0.88 (t, *J* = 6.6 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz $CDCl_3$): δ = 152.9, 149.3, 144.1, 133.2, 130.9, 130.8, 127.8, 127.4, 120.9, 112.1, 111.4, 69.6, 69.3, 49.6, 44.2, 32.0, 29.8, 29.5, 29.2, 29.1, 26.1, 22.8, 14.2 ppm. IR (ATR): $\tilde{\nu}$ = 3272, 2918, 2849, 2359, 1586, 1510, 1322.1263, 1137, 1091, 629 cm^{-1}. MALDI-TOF MS (dithranol): *m*/*z* calcd. for $C_{75}H_{124}N_4O_{10}S_3$ [M]$^+$ 1336.9; found 1337.8 [M]$^+$, 1359.8 [M + Na]$^+$, 1375.8 [M + K]$^+$. $C_{75}H_{124}N_4O_{10}S_3$ (1338.01): calcd. C 67.32, H 9.34, N 4.19; found C 67.48, H 9.56, N 4.33.

(*E*,*E*)-6-[(4-Aminophenyl)sulfonyl]-1,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene (6c): Isolated yield: 0.54 g (91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.3 Hz, 2 H), 7.42 (dd, *J* = 8.3, 2.0 Hz, 2 H), 7.31 (d, *J* = 2.0 Hz, 2 H), 6.90 (d, *J* = 8.3 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 5.54 (br. s, 4 H), 4.75 (t, *J* = 6.4 Hz, 2 H, NH), 4.15 (br. s, 2 H, NH_2), 4.03 (t, *J* = 6.6 Hz, 4 H), 3.98 (t, *J* = 6.6 Hz, 4 H), 3.65 (m, 4 H), 3.46 (m, 4 H), 1.85–1.75 (complex signal group, 8 H), 1.38–1.22 (complex signal group, 72 H), 0.87 (t, *J* = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz $CDCl_3$): δ = 152.9, 150.7, 149.3, 131.1, 129.5, 128.6, 127.9, 121.0, 114.3, 112.3, 111.6, 69.7, 69.4, 68.1, 49.3, 44.5, 32.1, 29.8, 29.5, 29.3, 29.1, 26.1, 25.8, 22.8, 14.3 ppm. IR (ATR): $\tilde{\nu}$ = 3491, 3381, 3272, 2917, 2849, 1742, 1586, 1317, 1135, 736, 679 cm^{-1}. $C_{74}H_{126}N_4O_{10}S_3$ (1328.01): calcd. C 66.93, H 9.56, N 4.22, S 7.24; found C 66.80 and 66.85, H 9.68 and 9.70, N 4.30 and 4.34, S 6.80 and 6.75.

(*E*,*E*)-1,11-Bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-6-(phenylsulfonyl)-1,6,11-triazaundeca-3,8-diene (6d): Isolated yield: 0.36 g (95%). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.1 Hz, 2 H), 7.54 (m, 3 H), 7.42 (dd, *J* = 8.5, 2.0 Hz, 2 H), 7.34 (d, *J* = 2.0 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 5.53 (m, 4 H), 5.24 (t, *J* = 6.2 Hz, 2 H, NH), 4.02 (t, *J* = 6.5 Hz, 4 H), 3.96 (t, *J* = 6.4 Hz, 4 H), 3.69. (d, *J* = 5.5 Hz, 4 H), 3.46 (t, *J* = 5.2 Hz, 4 H), 1.91–1.71 (complex signal group, 8 H), 1.50–1.26 (complex signal group, 72 H), 0.89 (t, *J* = 6.4 Hz, 12 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 152.7, 149.1, 139,7, 130.8, 129.9, 129.2, 127.9, 127.1, 120.9, 112.0, 111.3, 111.2, 69.4, 69.2, 49.0, 44.3, 31.9, 29.8, 29.7, 29.67, 29.6, 29.5, 29.4, 29.38, 29.1, 29.0, 26.0, 22.7, 14.2, 14.1 ppm. IR (ATR): $\tilde{\nu}$ = 3273, 2919, 2850, 1586, 1509, 1464, 1414, 1393, 1320, 1263, 1232, 1153, 1135, 1090, 1047, 1022, 1001, 987, 969, 848, 761, 688, 677, 621 cm^{-1}. HR-MALDI-TOF MS (dithranol/NaTFA): *m*/*z* calcd. for $C_{74}H_{125}N_3O_{10}S_3$ [M]$^+$ 1311.853; found 1334.839 [M + Na]$^+$.

Synthesis of Macrocycles 7: Compounds **7b** and **7d** were obtained by following the same experimental procedure described for **7a** (Scheme 2).

(*E*,*E*,*E*)-1,6-Bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-11-[(4-fluoro-phenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (7a): To a suspension of K_2CO_3 (0.30 g, 2.20 mmol) in CH_3CN/THF (60 mL/25 mL) heated to reflux was slowly added a solution of **6a** (0.49 g, 0.37 mmol) and (2*E*)-1,4-dibromo-2-butene (0.09 g. 0.40 mmol) in CH_3CN/THF (40 mL/15 mL). After the addition, the mixture was heated to reflux for 24 h. The salts were filtered off, and the solid was washed with hot CH_3CN. The solvent from the filtrates was evaporated and the residue was purified by column chromatography (hexane/EtOAc, 8:2) to give **7a**, yield 0.37 g (73%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 8.9, $J_{H,F}$ = 5.1 Hz, 2 H), 7.31 (dd, *J* = 8.4, $J_{H,F}$ = 1.9 Hz, 2 H), 7.14 (m, 4 H), 6.91 (d, *J* = 8.5 Hz, 2 H), 4.01 (q, *J* = 6.7 Hz, 8 H), 5.58 (s, 6 H), 3.66 (s, 12 H), 1.81 (s, 8 H), 1.43 (m, 8 H), 1.25 (complex signal group, 64 H), 0.86 (t, *J* = 6.3 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C,F}$ = 255.1 Hz), 153.0, 149.2, 135.4 (d, $J_{C,F}$ = 2.6 Hz), 130.3, 130.0, 129.8 (d, $J_{C,F}$ = 9.5 Hz), 129.6, 129.1, 121.0, 116.3 (d, $J_{C,F}$ = 22.6 Hz), 112.4, 111.8, 69.6, 69.3, 50.8, 50.7, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 26.0, 22.7, 21.2, 14.2 ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = 105.6 ppm. IR (ATR): $\tilde{\nu}$ =2920, 2851, 1587, 1508, 1466, 1329, 1261, 1230, 1139, 1091, 904 cm^{-1}. MS (MALDI$^+$) (dithranol): *m*/*z* calcd. for $C_{78}H_{128}FN_3O_{10}S_3$ [M]$^+$ 1381.87; found 1404.9 [M + Na]$^+$. $C_{78}H_{128}FN_3O_{10}S_3$ (1383.06): calcd. C 67.74, H 9.33, N 3.04; found C 67.91, H 9.14, N 3.13.

(*E*,*E*,*E*)-1-[(4-Cyanophenyl)sulfonyl]-6,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene (7b): Compound **7b** was not purified by column chromatography. The residue obtained after evaporation of the solvent was suspended in a mixture of diethyl ether/methanol (1:1), then filtered and dried to obtain pure compound **7b**. Isolated yield: 0.04 g (50%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.89 (app. d, *J* = 8.5 Hz, 2 H), 7.86 (app. d, *J* = 8.5 Hz, 2 H), 7.33 (dd, *J* = 8.4, 2.1 Hz, 2 H), 7.22 (d, *J* = 2.1 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 5.63 (s, 6 H), 4.04 (t, *J* = 6.8 Hz, 4 H), 4.01 (t, *J* = 6.5 Hz, 4 H), 3.75 (d, *J* = 4.7 Hz, 4 H), 3.66 (s, 8 H), 1.95–1.68 (m, 8 H), 1.54–1.39 (m, 8 H), 1.27 (s, 64 H), 0.88 (t, *J* = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz $CDCl_3$): δ = 153.2, 149.4, 144.0, 133.2, 130.8, 130.4, 129.9, 128.6, 127.9, 121.2, 117.4, 116.6, 112.6, 112.2, 69.9, 69.5, 51.1, 50.9, 50.7, 32.1, 28.83, 29.79, 29.6, 29.5, 29.3, 29.2, 26.2, 22.8, 14.2 ppm. IR (ATR): $\tilde{\nu}$ = 2920, 2851, 2231, 1586, 1508, 1329, 1261, 1155, 1137, 1090, 906, 721 cm^{-1}. MALDI-TOF MS (dithranol): calcd. for $C_{79}H_{128}N_4O_{10}S_3$ [M]$^+$ 1388.9; found 1412.8, [M + Na]$^+$. $C_{79}H_{128}N_4O_{10}S_3$ (1390.08): calcd. C 68.26, H 9.28, N 4.03, S 6.92; found C 67.95, H 9.30, N 3.75, S 6.68.

(*E*,*E*,*E*)-1,6-Bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-11-(phenyl)sulfonyl-1,6,11-triazacyclopentadeca-3,8,13-triene (7d): Isolated yield: 0.14 g (54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.1 Hz, 2 H), 7.58 (m, 3 H), 7.35 (dd, *J* = 8.5, 2.0 Hz, 2 H), 7.24 (d, *J* = 2.0 Hz, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 5.56 (s, 6 H), 4.05 (dd, *J* = 15.0, 6.5 Hz, 8 H), 3.69 (s, 12 H), 1.93–1.78 (complex signal group, 8 H), 1.57–1.17 (complex signal group, 72 H), 0.90 (t, *J* = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 153.2, 149.5, 139.5, 133.1, 130.6, 130.1, 130.0, 129.7, 129.6, 127.5, 121.3, 112.7, 112.2, 70.0, 69.6, 51.2, 32.3, 30.11, 30.10, 30.07, 30.0, 29.83, 29.8, 29.6, 29.4, 26.4, 26.39, 23.1, 14.5 ppm. IR (ATR): $\tilde{\nu}$ = 2921, 2852, 1586, 1508, 1467, 1446, 1412, 1330, 1261, 1231, 1156, 1138, 1092, 971, 908, 625 cm^{-1}. HR-MALDI-TOF MS (dithranol/NaTFA): *m*/*z* calcd. for $C_{78}H_{129}N_3O_{10}S_3$ [M]$^+$ 1363.884; found 1386.873 [M + Na]$^+$.

Compound 7c: Prepared by following the method outlined in Scheme 3.

(*E*)-*N*,*N*′-Bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-2-buten-1,4-diamine (8): Compound **2** (2.63 g, 4.20 mmol) was dissolved in anhydrous CH_3CN (100 mL), and (*E*)-1,4-dibromo-2-butene (0.46 g, 2.10 mmol) and K_2CO_3 (1.74 g, 12.6 mmol) were added. The mix-

ture was stirred overnight, then the salts were filtered off before the reaction mixture had cooled. Salts were washed twice with anhydrous CH_3CN. The CH_3CN solution was evaporated and **8** (protected with Boc groups) was isolated, yield 2.68 g (98%); m.p. 71–73 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.44 (dd, J = 8.5, 2.2 Hz, 2 H), 7.40 (d, J = 2.2 Hz, 2 H), 6.88 (d, J = 8.5 Hz, 2 H), 5.92–5.88 (m, 2 H), 4.43 (br. s, 4 H), 4.01 (t, J = 6.5 Hz, 8 H), 1.94–1.70 (m, 8 H), 1.34 (s, 18 H), 1.58–1.26 (complex signal group, 72 H), 0.88 (t, J = 6.6 Hz, 12 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 153.2, 150.7, 148.3, 131.24, 129.16, 122.0, 112.9, 111.9, 84.1, 77.4, 77.0, 76.7, 69.6, 69.2, 47.6, 31.9, 29.7, 29.67, 29.63, 29.41, 29.38, 29.1, 27.9, 25.98, 25.96, 22.7, 14.1 ppm. IR (ATR): $\tilde{\nu}$ = 2916, 2849, 1732, 1585, 1418, 1245, 1141, 717 cm^{-1}. $C_{74}H_{130}N_2O_{12}S$ (1271.91): calcd. C 68.16, H 10.05, N 2.15; found C 68.32 and 68.07, H 10.26 and 10.06, N 2.12 and 2.14.

Protected compound **8** (2.65 g, 0.16 mmol) was dissolved in CH_2Cl_2 (5 mL) and an excess of TFA (4 mL) was added. The mixture was stirred for 6 h and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (15 mL) and extracted with water (3 × 15 mL). The organic phase was dried with anhydrous Na_2SO_4, filtered, and the filtrate was evaporated. The residue was purified by column chromatography (hexane/EtOAc, 7:3) to give **8** (0.35 g, 96%) as a white solid; m.p. 110–112 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39 (dd, J = 8.5, 2.2 Hz, 2 H), 7.29 (d, J = 2.2 Hz, 2 H), 6.91 (d, J = 8.5 Hz, 2 H), 5.54 (t, J = 2.9 Hz, 2 H), 4.43 (t, J = 6.2 Hz, 2 H, NH), 4.02 (m, 8 H), 3.48 (m, 4 H), 2.02–1.75 (m, 8 H), 1.55–1.14 (m, 72 H), 0.88 (t, J = 6.6 Hz, 12 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 153.2, 149.4, 131.4, 128.9, 121.2, 112.6, 112.3, 77.5, 77.2, 76.8, 69.95, 65.55, 44.67, 32.07, 29.83, 29.80, 29.76, 29.6, 29.53, 29.49, 29.4, 29.3, 26.1, 22.8, 14.2 ppm. IR (ATR): $\tilde{\nu}$ = 3325, 3271, 2954, 2916, 2848, 1585, 1509, 1469, 1319, 1263, 1231, 1135, 718 cm^{-1}. $C_{64}H_{114}N_2O_8S_2$ (1103.73): calcd. C 69.64, H 10.41, N 2.54; found C 69.61 and 69.85, H 10.52 and 10.52, N 2.43 and 2.54.

(*E*,*E*,*E*)-1,14-Dibromo-5,10-bis{[(3,4-didodecyloxy)phenyl]sulfonyl}-5,10-diazatetradeca-2,7,12-triene (9): Compound **8** (0.20 g, 0.18 mmol) was dissolved in a hot mixture of CH_3CN/THF (2:1, 6 mL), and K_2CO_3 (0.12 g, 0.90 mmol) was added. The suspension was stirred at 60 °C for 15 min, then (*E*)-1,4-dibromo-2-butene (0.46 g, 2.20 mmol) was added to the mixture, which was heated to reflux overnight. Salts were filtered off and the filtrate was evaporated. The residue was washed three times with a mixture of diethyl ether/methanol (1:1), filtered, and dried. Compound **9** (0.21 g, 56% yield) was isolated in almost pure form, but could not be purified further by column chromatography due to its low stability in the presence of silica gel and alumina. This compound was used in the preparation of compound **7c**, m.p. 72–78 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.31 (dd, J = 8.5, 2.1 Hz, 2 H), 7.21 (d, J = 2.1 Hz, 2 H), 6.92 (d, J = 8.5 Hz, 2 H), 5.77 (dt, J = 15.7, 6.0 Hz, 2 H), 5.55 (dt, J = 15.3, 6.9 Hz, 2 H), 5.50 (br. s, 2 H), 4.01 (m, 8 H), 3.85 (d, J = 8.5 Hz, 4 H), 3.72–3.60 (complex signal group, 8 H), 1.81 (m, 2 H), 1.75–1.25 (complex signal group, 68 H), 0.87 (t, J = 6.6 Hz, 12 H) ppm. ^{13}C NMR (100.5 MHz $CDCl_3$): δ = 153.3, 149.5, 131.5, 130.9, 130.2, 129.8, 121.4, 112.8, 112.4, 70.1, 69.7, 49.0, 48.7, 32.3, 31.7, 30.1, 30.04, 30.01, 29.8, 29.7, 29.6, 29.5, 26.4, 23.1, 14.5 ppm. IR (ATR): $\tilde{\nu}$ = 2917, 2849, 1720, 1586, 1509, 1329, 1261, 1139, 799, 721 cm^{-1}. This compound could not be analyzed by HRMS (MALDI-TOF or ESI techniques), or elemental analysis due to its instability.

(*E*,*E*,*E*)-1-[(4-Aminophenyl)sulfonyl]-6,11-bis{[(3,4-didodecyloxy)-phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene (7c): K_2CO_3 (0.06 g, 0.40 mmol) was added to hot CH_3CN (10 mL), and compound **9** (0.10 g, 0.07 mmol) was then added. The mixture was heated at 70 °C for 15 min, then a solution of sulfonamide **4c** (0.01 g, 0.07 mmol) in CH_3CN/THF (3:2, 10 mL) was added dropwise over 2 h. The mixture was heated to reflux overnight, then the salts were filtered off and washed with the same mixture of hot solvents. Filtrates were evaporated and the residue was purified by column chromatography (hexane/EtOAc, 8:2) to give **7c** (0.06 g, 60%), m.p. 56 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.3 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.22 (s, 2 H), 6.92 (d, J = 8.5 Hz, 2 H), 6.68 (d, J = 8.3 Hz, 2 H), 5.59 (s, 6 H), 4.13 (br. s, 2 H, NH_2), 4.02 (m, 8 H), 3.65 (s, 12 H), 1.83–1.72 (complex signal group, 8 H), 1.60–1.06 (complex signal group, 72 H), 0.88 (t, J = 6.5 Hz, 12 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 153.0, 150.7, 149.2, 130.3, 129.9, 129.7, 129.5, 121.1, 114.3, 112.4, 112.0, 69.8, 69.4, 50.92, 50.88, 32.1, 29.9, 29.84, 29.81, 29.77, 29.6, 29.5, 29.3, 29.2, 26.14, 26.12, 14.3 ppm. IR (ATR): $\tilde{\nu}$ = 2918, 2850, 1588, 1509, 1323, 1259, 1014, 863, 794, 673 cm^{-1}. MALDI-TOF MS (DCTB/NaTFA): *m/z* calcd. for $C_{78}H_{130}N_4O_{10}S_3$ $[M]^+$ 1379.1; found 1402.1 $[M + Na]^+$. $C_{78}H_{130}N_4O_{10}S_3$ (1380.09): calcd. C 67.88, H 9.49, N 4.06; found C 68.02, H 9.53, N 4.31.

Supporting Information (see footnote on the first page of this article): Contains ^{1}H and ^{13}C NMR spectra of previously reported compound **1**–**3**, ^{1}H, ^{13}C and ^{19}F NMR spectra, IR spectra, and some MS experiments for the new compounds (**5a**–**d**, **6a**–**d**, **7a**–**d**, **8** and **9**). DSC thermograms are also gathered for compounds **6a**–**d** and **7a**, **7b**, and **7d**.

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[18] Concerning the intensity of the peaks, diffraction theory shows that the amplitude of the wave scattered $F(Q)$ is given by the Fourier transform of the "structure". For X-rays, the "structure" means the electron density distribution within the sample, $\rho(r)$. The observed intensity is then the modulus-squared of the amplitude: $I(Q) = |F(Q)|^2$.

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