# Insight into the mesogenic character of 15-membered triolefinic azamacrocycles, and their diolefinic open precursors and Pd(0) complexes†

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The mesogenic ability of triolefinic 15-membered azamacrocycles, appropriately functionalised with arenesulfonamide groups, as well as their open precursors and palladium(0) complexes, has been explored. The double bonds increase the rigidity of the macrocycle and are also responsible for the coordination to the metal. These features, along with the substitution pattern of the aryl units, determine the mesomorphic behaviour of the compounds. For example, a smectic mesophase was observed for the macrocycle derived from 4-hexadecyloxybenzenesulfonamides. In contrast, columnar mesophases appear for derivatives that incorporate 3,4-dialkoxybenzenesulfonamides. All of the mesophases were studied by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction, which enabled the determination of the structural parameters.

## Introduction

It is widely recognized that liquid crystals offer a unique type of control over molecular orientation and position.[1] Such a self-organization process is a convenient tool in the search for functional materials. Indeed, this phenomenon allows molecular building blocks, which can also bear functionality inherent to their chemical structure, to arrange within the bulk in a controlled and defined disposition.

In this respect we have explored the mesogenic properties of suitably designed triolefinic 15-membered azamacrocycles. These azamacrocycles are excellent ligands for Pd(0), Pt(0) and, to a lesser extent, Ag(I). The palladium complexes are good catalysts for many carbon–carbon bond forming reactions and these catalytic systems are frequently recovered. On considering the molecular structure, it is remarkable that the three olefins are the active coordination sites and the nitrogen atoms do not coordinate at all. Their presence in the macrocycle is imposed by the availability of numerous arenesulfonamides and by their excellent reactivity towards 1,4-dibromo-2-butenes. Moreover, the nitrogen atoms support a broad variety of arenesulfonyl groups that provide certain properties: electrochemical properties [ferrocenyl, 4-(1-pyrrolylphenyl)], solubility in chosen solvents (2,4,6-triisopropylphenyl and 4-perfluoroalkylphenyl), crystallinity (*p*-tolyl) and colour, which allows spotting in chromatography (ferrocenyl), *etc.*[2] The versatility in the methods of preparation of this family of azamacrocycles, as well as the almost endless ability to introduce various functional groups into the arenesulfonamide moieties, led us to introduce chains of different lengths in an attempt to promote liquid crystalline behaviour. Mesomorphic behaviour would provide supramolecular arrangements that could give rise to macroscopically ordered materials.

Examples of azamacrocyclic liquid crystals have already been described. For example, saturated N-acylated azacoronands and some of their metal complexes have been reported to display either calamitic or columnar mesomorphism depending on the flexibility of the central core.[3] Furthermore, of the conjugated nitrogen-containing macrocycles,[4] phthalocyanine and porphyrin derivatives are two of the most widely studied mesogenic systems that are able to organize themselves into columnar mesophases.[5]

In the work described here we synthesized novel 15-membered triolefinic azamacrocycles functionalized with appropriate arenesulfonamide groups (Scheme 1). In these compounds, the double bonds increase the rigidity of the cycles and are also responsible for coordination to the metal. In order to assess the potential of these macrocycles as mesogenic cores, derivatives with long alkoxy tails surrounding the azamacrocycle were designed. In this way all three nitrogen atoms in the macrocycle were functionalised by the incorporation of benzenesulfonic groups, which allowed us to introduce one terminal chain in position 4 (series a), two chains in positions 3 and 4 (series b and c) and three terminal chains in positions 2, 3 and 4 (series d). Examination of the synthetic pathway for the complexes (Scheme 1), as well as previously described N-acylated macrocycle open-analogues,[6] led us to envisage that some intermediate products could meet the structural requirements for liquid crystalline properties. Thus, the compounds with all three substitution patterns in the benzene ring were investigated in terms of the thermal behaviour of the corresponding open precursors (**1a–d**), the triolefinic macrocycles (**2a–d**) and the Pd complexes (**3a–d**).

## Results and discussion

### Synthesis

The synthetic route used to prepare compounds **1**, **2**, and **3** (series **a**, **b**, **c** and **d**) is shown in Scheme 1.[2] Macrocycles **2a–d** were prepared by controlled condensations between

† Electronic supplementary information (ESI) available: spacings observed in the X-ray diffraction studies of the mesogenic compounds. See http://www.rsc.org/suppdata/jm/b5/b502561c/

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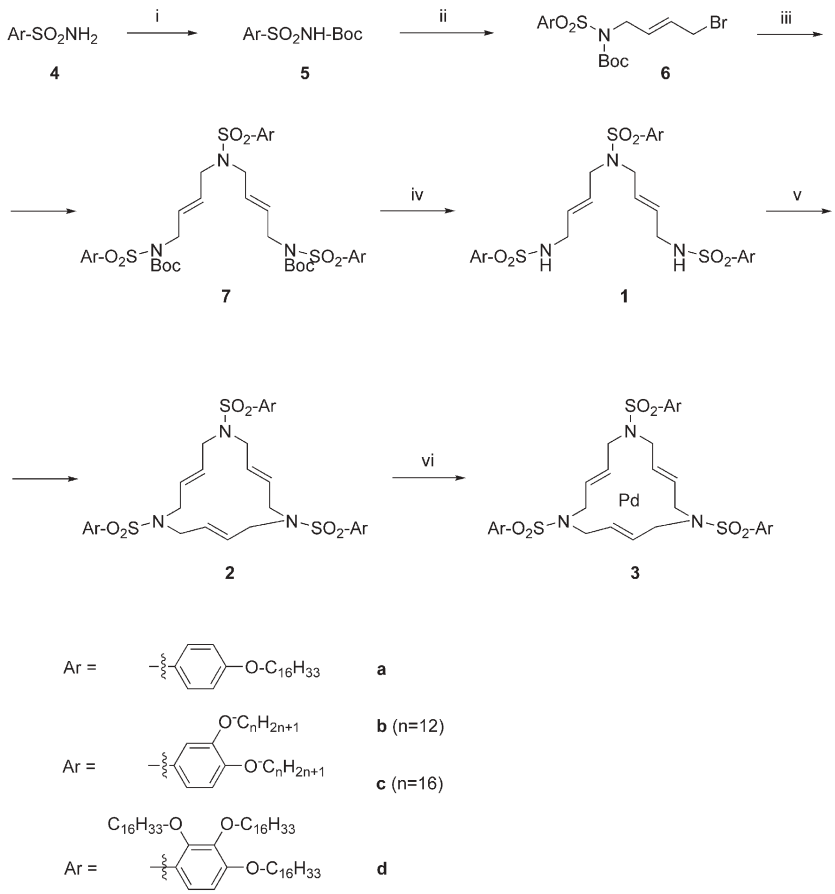


**Scheme 1** Preparation of **1**, **2** and **3**. *Reagents and conditions:* i $(t\text{-BuO-CO})_2O$, DMAP, dichloromethane; ii *trans*-1,4-dibromobutene (4 equiv.), $K_2CO_3$, $CH_3CN$ (reflux); iii **4** (0.5 equiv.), $K_2CO_3$, $CH_3CN$ (reflux); iv TFAA, dichloromethane; direct transformation of **6c** + **4c** into **1c** can be achieved in 49% yield using NaH in DMF; v *trans*-1,4-dibromobutene (1 equiv.), $K_2CO_3$, THF or THF–$CH_3CN$; vi $Pd(PPh_3)_4$ or $Pd(dba)_2$ in THF, 50 °C.

*trans*-1,4-dibromo-2-butene with Boc-protected arenesulfonamides **5** in the first step to afford **6**, and with bissulfonamides **1** in the last step. Compounds of series **a–d** are extremely hydrophobic and difficult to manipulate. These difficulties explain the low chemical yields obtained in some of the steps, although the cyclisation step works well and the formation of higher rings and polymers is not a problem. Palladium(0) complexes (**3**) were prepared by metal exchange from normal palladium(0) sources (Scheme 1). In these complexes (**3**) the nitrogen atoms are non-coordinating, with the coordinating ability being concentrated on the olefinic moieties.

## Mesomorphic behaviour

The thermal behaviour of all compounds was studied by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). The data are gathered in Table 1.

The presence of a single terminal alkoxy tail in each benzene ring promotes mesomorphic behaviour only in azamacrocycle **2a**. This compound exhibits an SmC mesophase, as indicated by the texture in Fig. 1a. Neither the open precursor nor the palladium(0) complex show liquid crystalline properties. It is reasonable to believe that the additional forces promoted by intermolecular H-bonds in the precursor and by the metal–metal interactions in the complex increase the melting point and preclude the appearance of mesomorphic behaviour.

The presence of two tails in each aromatic ring gives rise to a significant tendency for the molecules to self-organize into columnar mesophases, but this tendency is influenced by the

**Table 1** Thermal and thermodynamic properties calculated during the second heating-cooling cycle. Temperatures are given in °C. Enthalpies are given in kJ $mol^{-1}$ and appear in parentheses

| Compound | Thermal and thermodynamic behaviour | | | | |
|---|---|---|---|---|---|
| **1a** | C | 104.3 (98.2) | I | | |
| **2a** | C | 49.3 (38.4) | SmC | 57.8 (2.8) | I |
| **3a** | C | 150.8 (37.2) | I | | |
| **1b** | C | 53.0 (64.1) | $Col_h$ | 70.6 (1.6) | I |
| **2b** | C | 45.3 (40.4)[a] | $Col_h$ | 46.7 (2.0)[b] | I |
| **3b** | C | 54.3 (7.5)[c] | $Col_r$ | 72.4 (2.5) | I |
| **1c** | C | 62.7 (123.9) | $Col_h$ | 76.7 (1.8) | I |
| **2c** | C | 68.4 (147.1) | I | | |
| **3c** | C | 63.9 (85.1) | I | | |
| **1d** | C | 41.0 (202.8) | I | | |
| **2d** | C | 37.9 (180.3) | I | | |
| **3d** | C | 34.9 (160.6) | I | | |

[a] This value corresponds to the total enthalpy of the two transitions. The melting and clearing processes appear as overlapped peaks in the DSC heating scan. [b] This value was calculated from the cooling scan. [c] This enthalpy value corresponds to the coexistence of the crystal and the $Col_r$ mesophase.

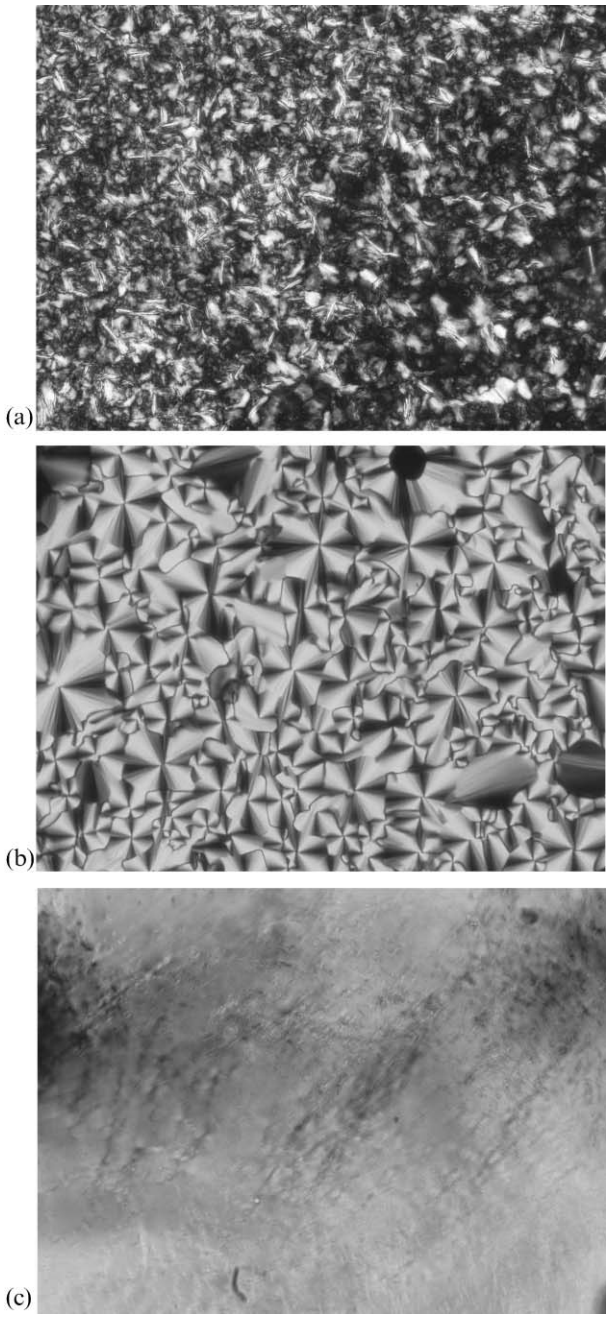


**Fig. 1** Photomicrographs of the textures observed by polarising optical microscopy on cooling from the isotropic state: a) compound **1a** SmC mesophase at 50 °C; b) compound **1b** $Col_h$ mesophase at 65 °C; c) compound **3b** $Col_r$ mesophase at 60 °C.

structure of the central part of the mesogenic molecule. The open precursors **1b** and **1c** both show mesomorphic behaviour. The focal-conic texture of their mesophase, as it appears on cooling from the isotropic state (Fig. 1b), corresponds unequivocally to a hexagonal columnar organization. Closing the molecule with a third olefinic unit gives rise to triolefinic azamacrocycles that are either devoid of mesomorphic character, *e.g.*, **2c**, or are mesomorphic over a short range, *e.g.*, **2b**. Macrocycle **2b** also shows a hexagonal columnar mesophase, as identified by POM. This situation is in contrast to that described for 1,4,7-triaazacyclononanes, which are more flexible saturated macrocycles and show lamellar mesomorphism when they are substituted with three 3,4-dialkoxyphenyl groups.[3g] Double bonds within the macrocycle must increase the rigidity of the system and this may give rise to a disk-like molecular shape that gives rise to columnar mesomorphism with a well-defined bidimensional arrangement. The palladium complex **3b** shows a rectangular columnar mesophase, which is very viscous and shows an ill-defined texture by POM (Fig. 1c). This compound shows a melting process with low enthalpy value, as measured by DSC.

Compounds of series **d** show unexpected thermal behaviour. All three compounds in this series have a crystalline state that melts directly into the isotropic liquid on heating. The 2,3,4-trisubstitution pattern in the benzenesulfonamide does not promote mesomorphic behaviour—in contrast to 3,4-disubstitution. The terminal chains must have great importance in terms of the intermolecular interactions in the crystal structure, as can be deduced from the high enthalpy values of the melting processes.

### X-Ray diffraction

X-Ray diffraction studies were performed on the liquid crystal phases of all the mesogenic compounds, except **2b** on account of its short thermal mesophase range.

The X-ray patterns confirm that the mesophase of **2a** is SmC, and the measured layer spacing is 36 Å (Table 2). This parameter is consistent with a single-layer arrangement of molecules. The molecular length estimated from Dreiding stereomodels for a fully-extended conformation is about 62 Å. In this estimation we considered that the molecules adopt a conformation in which the three 4-hexadecyloxyphenyl groups lie parallel to one another in such a way that one of these branches is oriented to the opposite side with respect to the other two (fork-like conformation, Fig. 2).[7] The difference between the experimentally measured layer thickness and the theoretical value is not unexpected for two reasons: (i) in an SmC mesophase the molecules are tilted; (ii) in all the fluid mesophases the hydrocarbon chains are in a molten state. These two effects lead to a significant decrease in the resulting layer thickness when compared to the predicted molecular length. Within the layers the molecules are arranged with an up-and-down statistical distribution of tilted, fork-like molecules.

The X-ray patterns of the compounds bearing six terminal chains (two alkoxy groups per ring) indicate that both open

**Table 2** Structural data for the mesophases measured by X-ray diffraction. The columns list, respectively, the compound number, the temperature of the experiment, the mesophase type, and the measured parameters (*d*: layer thickness in the SmC phase; *a*, *b*: lattice constants in the columnar mesophases)

| Compound | Temperature/°C | Mesophase | Parameters/Å |
|---|---|---|---|
| **2a** | 55 | SmC | $d = 36$ |
| **1c** | 75 | $Col_h$ | $a = 39.6$ |
| **1b** | 61 | $Col_h$ | $a = 35.6$ |
| **3b** | 65 | $Col_r$ | $a = 68.6$<br>$b = 27.6$ |

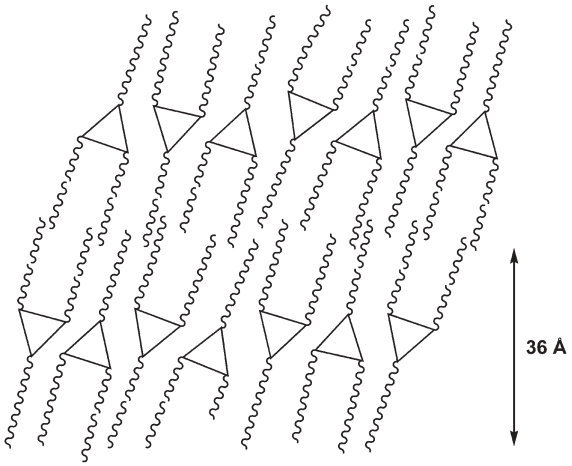


**Fig. 2** Simplified smectic model for the SmC phase of the azamacrocycle **2a**.

precursors **1c** and **1b** show a hexagonal columnar ($Col_h$) mesophase. The hexagonal lattice constants $a$ are 39.6 Å and 35.6 Å, respectively (Table 2). The difference of 4 Å is reasonable bearing in mind the different lengths of the peripheral chains. Moreover, from the measured lattice constant, the column cross section can be calculated as $S = a^2\sqrt{3}/2$. The values obtained are 1358 Å$^2$ for **1c** and 1096.5 Å$^2$ for **1b**. These values are too large for stacking of single molecules and are consistent with a dimeric structure in which associated pairs of molecules form the stack (Fig. 3). The relationship between the density $\rho$ of the compounds and the number $Z$ of molecules in the unit cell is given by the following equation:

$$\rho = (M/N)/(V/Z)$$

where $M$ is the molar mass (g), $N$ the Avogadro number, and $V$ the unit cell volume (cm$^3$). From the previous equation $Z$ can be deduced as

$$Z = (\rho VN)/M$$

and $V$ (in cm$^3$) is calculated by the formula $V = (\sqrt{3}/2)a^2c \times 10^{-24}$ for a hexagonal lattice, and $V = abc \times 10^{-24}$ for a rectangular lattice, where $a$, $b$, $c$ are the lattice constants in Å. Considering a density equal to 1 g cm$^{-3}$, this means that in the proposed hexagonal columnar structure the mean stacking distance ($c$ constant) between molecular pairs would be about 4.9 Å for **1c** and 5.1 Å for **1b** for $Z = 2$. These distances are reasonable compared to those found in other columnar mesophases. However their values cannot be experimentally confirmed due to the absence in the X-ray patterns of a maximum arising from the stacking periodicity. It can be deduced from this observation that there is no long-range order along the columnar axis in the mesophase of these compounds (*i.e.* these columnar mesophases are *disordered*). However, the estimated stacking distances are in fair agreement with those usually found in columnar liquid crystals.

It is possible that the proposed pairwise intermolecular association is induced by hydrogen-bonding interactions between the sulfonamide groups. The resulting dimers bear a

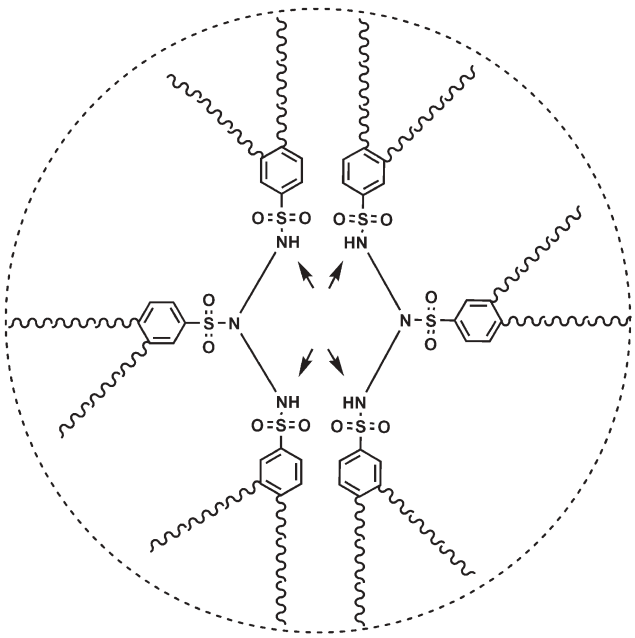

**Fig. 3** Simplified dimeric model for the open precursors **1b** and **1c** with different possibilities for H-bond interactions between the sulfonamide groups marked with an arrow.

total number of twelve peripheral chains, and these chains are able to fully surround the dimeric core by curling in order to fill efficiently the outer part of the columns. Alternatively, one could also consider another kind of intermolecular association involving a polymer-like superstructure in which the sulfonamide groups of each molecule interact with different molecules. This supramolecular structure should be able to generate a columnar arrangement by winding itself around the column axis. In this structure, two adjacent molecules would be mutually rotated around the column axis and shifted by about 2.5 Å along this axis. The combination of rotation and shifting allows efficient packing. Nevertheless, the data reported here are not sufficient to give a more detailed description of the actual structure.

The presence of two dodecyloxy tails in each benzene ring favours the mesomorphic behaviour not only in the open precursor **1b** but also in the closed azamacrocycle **2b** and the Pd complex **3b**. The macrocycle **2b** shows a hexagonal columnar mesophase over a very narrow temperature range and this could not be examined with our X-ray set-up. The mesophase of the Pd complex **3b** yielded a more complex pattern than the columnar mesophases described for **1c** and **1b**. The pattern contains four sharp maxima in the small-angle region corresponding to spacings of 34.3 Å, 25.6 Å, 17.1 Å and 13.8 Å. These maxima can be indexed, respectively, as the (2 0), (1 1), (4 0) and (0 2) reflections from a two-dimensional rectangular lattice with $a = 68.6$ Å and $b = 27.6$ Å. The mesophase of this compound is therefore columnar rectangular. Assuming that there are two columns per unit cell, the deduced column cross section is $ab/2 = 947$ Å$^2$. This value compares well with the 1096.5 Å$^2$ found for the hexagonal columnar mesophase of the analogous compound **1b**. The smaller cross section found for **3b** can be accounted for by a molecular tilt

with respect to the column axis in the rectangular columnar mesophase, a well-known phenomenon that produces an elliptical cross section in the columns. The symmetry of the rectangular columnar packing is probably *c2mm*, as deduced from the absence of reflections with Miller indexes $h + k = 2n + 1$. This symmetry is also consistent with the fact that the lattice constant *a* is much larger than *b*, because in a columnar mesophase with *c2mm* symmetry the long axis of the ellipses (cross section of the columns in the *ab* plane) is oriented along *a*.

In a similar way to compounds **1b** and **1c**, a reasonable density value is estimated if we assume that the rectangular mesophase consists of stacks of disk-like entities formed from two molecules **3b**. In this case, hydrogen bonding is not possible and this sort of dimerization could well be related to a more efficient packing, in the sense that twelve peripheral tails are able to fill the outer surface of the columns. Although the low-temperature phase exhibited by this compound is crystalline in nature, the crystalline phase is mixed with a liquid crystal phase. This is indicated by the coexistence in the room-temperature patterns of diffraction maxima due to both phases. However the relative amount of each of them depends on the thermal history. The proportion of crystalline phase is very small when the compound is cooled very quickly from the mesophase, whereas the proportion of crystalline phase increases when the cooling rate is slower or when a frozen sample is left for several hours at room temperature. These results are consistent with DSC results.

## Conclusion

The investigation of the mesomorphic properties of triolefinic azamacrocycles has led to the discovery of different types of mesomorphism, the nature of which depends on the number of tails in the benzene ring of the arenesulfonamide groups. The presence of one terminal tail in each benzene ring promotes calamitic-like behaviour only for the closed macrocycle (**2a**). 2,3,4-Trisubstitution of the benzenesulfonamide group gives compounds that are not mesogenic. In contrast, 3,4-dialkoxybenzenesulfonamide derivatives lead to molecules that show columnar mesomorphism. In general, the three types of derivative, *i.e.* the open precursor **1** (**1b** and **1c** with two olefinic units), the triolefinic macrocycle **2b** and its palladium(0) complex **3b**, give rise to hexagonal or rectangular columnar arrangements. The columns consist, in all cases, of stacks of dimeric units formed by the association of the molecular components. This association seems to be more favourable in the open precursor due to the possibility of H-bonding interactions.

## Experimental

### Synthesis of arenesulfonamides 4a–d

The four benzenesulfonamides were prepared following the methodology described by Hanby and Rydon[8] from the corresponding easily prepared substituted benzenes, obtained by alkylation of the respective phenols (references: hexadecyloxybenzene,[9] 1,2-didodecyloxybenzene,[10] 1,2-dihexadecyloxybenzene,[11] 1,2,3-trihexadecyloxybenzene.[12] Compound **4a** was previously described (melting point and elemental analysis were given in ref. 8). Compounds **4b–d** are new compounds.

**Analytical data. Hexadecyloxybenzenesulfonamide, 4a.** Yield 73%. Mp 108 °C (lit. 111 °C[8]). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.9 Hz, 6H), 1.20–1.50 (m, 26H), 1.83 (m, 2H), 4.03 (t, $J$ = 6.5 Hz, 2H), 4.77 (s, 2H, $NH_2$), 6.99 (dm, $J$ = 8.9 Hz, 2H), 7.87 (dm, $J$ = 8.9 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 28.7, 29.1, 29.4, 31.7, 68.3, 114.4, 128.3, 133.1, 162.4. IR (neat) $\nu$/cm$^{-1}$: 3358, 3259, 2920, 2850, 1158. $C_{22}H_{39}NO_3S$ (397.62 g mol$^{-1}$).

**3,4-Bis(dodecyloxy)benzenesulfonamide, 4b.** Yield 70%. Mp 97–99 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 6H), 1.20–1.55 (complex absorption, 36H), 1.85 (m, 4H), 4.03 (t, $J$ = 6.6 Hz, 2H), 4.06 (t, $J$ = 6.6 Hz, 2H), 4.84 (br s, 2H, $NH_2$), 6.92 (d, $J$ = 8.4 Hz, 1H), 7.40 (d, $J$ = 2.3 Hz, 1H), 7.51 (dd, $J$ = 8.4 and 2.3 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 28.7, 28.8, 29.1, 29.34, 29.37, 29.4, 31.6, 69.0, 69.2, 110.7, 111.9, 119.7, 133.2, 148.8, 152.4. IR (neat) $\nu$/cm$^{-1}$: 3358, 3261, 2919, 2851, 1587, 1292, 1266, 1160, 1142. Anal. Calc. for $C_{30}H_{55}NO_4S$ (525.83 g mol$^{-1}$): C 68.53, H 10.54, N 2.66, S 6.10; Found: C 68.41, H 10.53, N 2.65, S 6.02%.

**3,4-Bis(hexadecyloxy)benzenesulfonamide, 4c.** Yield 83%. Mp 100–101 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 6H), 1.43 (br s, 48H), 1.49 (complex absorption, 4H), 1.85, (m, 4H), 4.03 (t, $J$ = 6.4 Hz, 2H), 4.06 (t, $J$ = 6.4 Hz, 2H), 4.76 (s, 2H, $NH_2$), 6.93 (d, $J$ = 8.5 Hz, 1H), 7.40 (d, $J$ = 2.2 Hz, 1H), 7.52 (dd, $J$ = 8.5 and 2.2 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.5, 23.1, 26.35, 26.37, 29.4, 29.5, 29.8, 30.0, 30.1, 30.13, 32.3, 32.4, 69.7, 69.9, 111.4, 112.5, 120.5, 133.7, 149.5, 153.2. IR (neat) $\nu$/cm$^{-1}$: 3356, 3258, 2917, 1267, 1144. Anal. Calc. for $C_{38}H_{71}NO_4S$ (638.05 g mol$^{-1}$): C 71.53, H 11.22, N 2.20, S 5.03; Found: C 71.52, H 11.26, N 2.21, S 4.62%.

**2,3,4-Tris(hexadecyloxy)benzenesulfonamide, 4d.** Yield 44%. Mp 86–87 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.8 Hz, 9H), 1.20–1.60 (complex absorption, 78H), 1.83 (complex absorption, 6H), 4.01 (t, $J$ = 6.5 Hz, 2H), 4.04 (t, $J$ = 6.4 Hz, 2H), 4.27 (t, $J$ = 6.9 Hz, 2H), 5.06 (br s, 2H, $NH_2$), 6.69 (d, $J$ = 8.8 Hz, 1H), 7.56 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.6, 25.8, 25.9, 28.9, 29.1, 29.2, 29.3, 29.35, 29.4, 29.45, 29.9, 30.1, 31.7, 68.8, 73.5, 75.0, 106.8, 122.3, 127.8, 141.9, 149.9, 157.3. IR (neat) $\nu$/cm$^{-1}$: 339, 3266, 2954, 2848, 1586, 1490, 1336, 1178, 1087. Anal. Calc. for $C_{54}H_{103}NO_5S$ (878.48 g mol$^{-1}$): C 73.83, H 11.82, N 1.59, S 3.65; Found: C 74.10, H 11.43, N 1.56, S 3.46%.

### Synthesis of *N*-(*tert*-butyloxycarbonyl)arenesulfonamides 5a–d

These new compounds were prepared according to the general method in ref. 13.

***N*-(*tert*-Butyloxycarbonyl)-4-(hexadecyloxy)benzenesulfonamide, 5a.** Yield 83%. Mp 57–58 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.3 Hz, 3H), 1.20–1.50 (m, 26H), 1.41 (s, 9H), 1.83 (m, 2H), 4.04 (t, $J$ = 6.6 Hz, 2H), 7.00 (dm,

 

$J$ = 9.0 Hz, 2H), 7.95 (dm, $J$ = 9.0 Hz 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 27.6, 28.8, 29.1, 29.27, 29.29, 29.37, 29.40, 31.7, 68.3, 83.6, 114.2, 129.8, 130.2, 149.0, 163.1. IR (neat) $\nu$/cm$^{-1}$: 3284, 2919, 1747, 1149. Anal. Calc. for $C_{27}H_{47}NO_5S$ (497.74 g mol$^{-1}$): C 65.15, H 9.52, N 2.81, S 6.44; Found: C 65.18, H 9.64, N 2.78, S 6.15%.

***N*-(*tert*-Butyloxycarbonyl)-3,4-bis(dodecyloxy)benzenesulfonamide, 5b.** Yield 86%. Mp 66–67 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 6H), 1.20–1.56 (complex absorption, 36 H), 1.41 (s, 9H), 1.86 (m, 4H), 4.05 (t, $J$ = 6.6 Hz, 2H), 4.07 (t, $J$ = 6.4 Hz, 2H), 6.94 (d, $J$ = 8.6 Hz, 1H), 7.48 (d, $J$ = 2.3 Hz, 1H), 7.60 (dd, $J$ = 8.6 and 2.3 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 27.6, 28.7, 28.8, 29.1, 29.33, 29.36, 29.40, 31.6, 68.9, 69.2, 83.5, 111.4, 112.2, 122.0, 129.8, 148.4, 149.0, 153.3. IR (neat) $\nu$cm$^{-1}$: 3347, 2915, 2848, 1742, 1585, 1132. Anal. Calc. for $C_{35}H_{63}NO_6S$ (625.95 g mol$^{-1}$): C 67.16, H 10.14, N 2.24, S 5.12; Found: C 67.22, H 10.13, N 2.19, S 4.98%.

***N*-(*tert*-Butyloxycarbonyl)-3,4-bis(hexadecyloxy)benzenesulfonamide, 5c.** Yield 89%. Mp 73 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 6H), 1.20–1.50 (complex absorption, 52 H), 1.41 (s, 9H), 1.87 (m, 4H), 4.05 (t, $J$ = 6.4 Hz, 2H), 4.07 (t, $J$ = 6.4 Hz, 2H), 6.94 (d, $J$ = 8.6 Hz, 1H), 7.47 (d, $J$ = 2.2 Hz, 1H), 7.60 (dd, $J$ = 8.6 and 2.2 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 27.6, 28.7, 28.8, 29.1, 29.11, 29.3, 29.4, 29.43, 31.7, 68.98, 69.03, 83.5, 111.5, 112.3, 122.1, 129.8, 148.5, 148.8, 153.4. IR (neat) $\nu$/cm$^{-1}$: 3295, 2917, 2849, 1745, 1131. Anal. Calc. for $C_{43}H_{79}NO_6S$ (738.17 g mol$^{-1}$): C 69.97, H 10.79, N 1.90, S 4.34; Found: C 69.83, H 11.51, N 1.84, S 4.30%.

***N*-(*tert*-Butyloxycarbonyl)-2,3,4-tris(hexadecyloxy)benzenesulfonamide, 5d.** Yield 98%. Mp 70–72 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 9H), 1.20–1.55 (complex absorption, 78 H), 1.37 (s, 9H), 1.80 (m, 6H), 3.96 (t, $J$ = 6.5 Hz, 2H), 4.04 (t, $J$ = 6.4 Hz, 2H), 4.23 (t, $J$ = 6.9 Hz, 2H), 6.72 (d, $J$ = 9.0 Hz, 1H), 7.16 (br s, 1H, NH), 7.70 (d, $J$ = 9.0 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.5, 23.1, 26.3, 26.47, 26.52, 28.2, 29.5, 29.8, 29.9, 29.98, 30.01, 30.04, 30.09, 30.13, 30.2, 30.6, 30.7, 32.3, 69.5, 74.2, 75.3, 83.9, 107.1, 124.2, 126.9, 142.3, 149.7, 151.6, 158.9. IR (neat) $\nu$/cm$^{-1}$: 3263, 3915, 2847, 1742, 1579, 1465, 1125, 1085. Anal. Calc. for $C_{59}H_{111}NO_7S$ (978.59 g mol$^{-1}$): C 72.41, H 11.43, N 1.43, S 3.28; Found: C 72.14, H 11.78, N 1.43, S 2.98%.

### Synthesis of *N*-[(*E*)-4-bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)arenesulfonamides 6a–d

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)-[4-(hexadecyloxy)]benzenesulfonamide, 6a. General procedure.** A stirred mixture of **5a** (2.00 g, 4.0 mmol), 1,4-dibromo-2-butene (3.54 g, 16.0 mmol), anhydrous potassium carbonate (2.78 g, 20.0 mmol) and acetonitrile (70 mL) was heated under reflux for 14 h. The salts were filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel with hexanes–diethyl ether (9.5 : 0.5) to afford **6a** (1.50 g, 59% yield) as a white solid. Mp 46–47 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.88 (t, $J$ = 6.5 Hz, 3H), 1.20–1.50 (complex absorption, 26H), 1.27 (s, 9H), 1.81 (m, 2H), 3.96 (d, $J$ = 6.9 Hz, 2H), 4.02 (t, $J$ = 6.5 Hz, 2H), 4.44 (d, $J$ = 5.6 Hz, 2H), 5.92 (m, 2H), 6.95 (d, $J$ = 9.0 Hz, 2H), 7.85 (d, $J$ = 9.0 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 27.7, 28.8, 29.1, 29.27, 29.30, 29.37, 29.40, 31.3, 31.7, 46.9, 68.3, 84.1, 114.0, 129.7, 130.0, 130.2, 130.8, 150.5, 162.8. IR (neat) $\nu$/cm$^{-1}$: 2921, 2850, 1724, 1157. Anal. Calc. for $C_{31}H_{52}BrNO_5S$ (630.73 g mol$^{-1}$): C 59.03, H 8.31, N 2.22, S 3.08; Found: C 59.01, H 8.36, N 2.21, S 3.91%.

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)-[3,4-bis(dodecyloxy)]benzenesulfonamide, 6b.** This compound was obtained in the same way as **6a**. Silica gel chromatography was performed with mixtures of hexanes–ethyl acetate of increasing polarity. Yield 68%. Colourless oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 6H), 1.20–1.56 (complex absorption, 36H), 1.39 (s, 9H), 1.85 (m, 4H), 3.98 (d, $J$ = 6.8 Hz, 2H), 4.04 (t, $J$ = 6.6 Hz, 2H), 4.07 (d, $J$ = 6.6 Hz, 2H), 4.45 (d, $J$ = 5.4 Hz, 2H), 5.91 (sept., 1H), 5.96 (sept. 1H), 6.92 (d, $J$ = 8.6 Hz, 1H), 7.39 (d, $J$ = 2.2 Hz, 2H), 7.50 (dd, $J$ = 8.6 and 2.2 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.65, 25.68, 27.6, 28.7, 28.8, 29.1, 29.31, 29.36, 29.39, 31.2, 31.6, 47.0, 69.0, 69.4, 84.0, 111.5, 112.7, 121.9, 129.6, 129.9, 130.9, 148.2, 150.4, 153.1. IR (neat) $\nu$/cm$^{-1}$: 2922, 2852, 1730, 1587, 1137, 632. Anal. Calc. for $C_{39}H_{68}BrNO_6S$ (758.94 g mol$^{-1}$): C 61.72, H 9.03, N 1.85, S 4.23; Found: C 61.76, H 9.01, N 1.81, S 4.13%.

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)-[3,4-bis(hexadecyloxy)]benzenesulfonamide, 6c.** This compound was obtained in the same way as **6a**. Silica gel chromatography was performed with mixtures of hexanes–ethyl acetate of increasing polarity. Yield 70%. Mp 34–35 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.4 Hz, 6H), 1.20–1.50 (complex absorption, 43H), 1.39 (s, 9H), 1.85 (m, 4H), 3.98 (d, $J$ = 6.2 Hz, 2H), 4.04 (t, $J$ = 6.8 Hz, 2H), 4.07 (d, $J$ = 7.0 Hz, 2H), 4.45 (d, $J$ = 5.4 Hz, 2H), 5.91 (sept., 1H), 5.96 (sept. 1H), 6.92 (d, $J$ = 8.2 Hz, 1H), 7.39 (d, $J$ = 1.3 Hz, 2H), 7.50 (dd, $J$ = 8.2 and 1.3 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.68, 25.71, 27.6, 28.7, 28.8, 29.1, 29.3, 29.38, 29.43, 31.2, 31.7, 47.0, 69.0, 69.4, 84.0, 111.5, 112.7, 121.9, 129.7, 129.9, 130.9, 148.2, 150.4, 153.1. IR (neat) $\nu$/cm$^{-1}$: 2915, 2848, 1727, 1137. Anal. Calc. for $C_{47}H_{84}BrNO_6S$ (871.15 g mol$^{-1}$): C 64.80, H 9.72, N 1.61, S 3.68; Found: C 64.77, H 9.74, N 1.58, S 3.49%.

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)-[2,3,4-tris(hexadecyloxy)]benzenesulfonamide, 6d.** This compound was obtained in the same way as **6a**, using mixtures of acetonitrile–tetrahydrofuran (THF) (9 : 1) as solvents. Silica gel chromatography was performed with hexanes–diethyl ether (9.5 : 0.5). Yield 76%. Mp 56–58 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 9H), 1.20–1.60 (complex absorption, 78H), 1.33 (s, 9H), 1.82 (m, 6H), 3.92–4.10 (complex absorption, 6H), 4.19 (t, $J$ = 7.2 Hz, 2H), 4.48 (d, $J$ = 4.2 Hz, 2H), 6.00 (complex absorption, 2H), 6.70 (d, $J$ = 9.0 Hz, 1H), 7.71 (d, $J$ = 9.0 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.5, 25.80, 25.83, 27.6, 28.0, 28.9, 29.1,

29.27, 29.32, 29.36, 29.42, 29.45, 30.0, 31.6, 31.7, 68.8, 73.6, 74.6, 83.5, 106.1, 124.9, 126.8, 128.7, 130.9, 141.5, 150.5, 151.0, 157.9. IR (neat) $\nu$/cm$^{-1}$: 2917, 2850, 1724, 1582, 1468, 1350, 1135, 1073. Anal. Calc. for $C_{63}H_{116}BrNO_7S$ (1111.58 g mol$^{-1}$): C 68.07, H 10.52, N 1.26, S 2.88; Found: C 68.15, H 10.65, N 1.08, S 2.64%.

### Synthesis of (*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,11-bis(*tert*-butyloxycarbonyl)-1,6,11-triazaundeca-3,8-dienes, 7a–d

**(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris{[4-(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 7a. General procedure.** A stirred mixture of sulfonamide **4a** (0.38 g, 0.95 mmol), bromosulfomanide **6a** (1.20 g, 1.9 mmol), anhydrous potassium carbonate (0.79 g, 5.7 mmol) and acetonitrile (30 mL) was heated under reflux for 14 h. The salts were filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel with hexanes–diethyl ether (9 : 1) to afford **7a** (1.22 g, 86% yield) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.5 Hz, 9H), 1.18–1.60 (complex absorption, 78H), 1.37 (s, 18H), 1.82 (m, 6H), 3.83 (d, $J$ = 5.9 Hz, 4H), 4.03 (t, $J$ = 6.5 Hz, 6H), 4.39 (d, $J$ = 5.6 Hz, 4H), 5.60 (dt, $J$ = 15.4 and 5.9 Hz, 2H), 5.76 (dt, $J$ = 15.4 and 5.6 Hz, 2H), 6.97 (d, $J$ = 8.9 Hz, 2H), 6.98 (d, $J$ = 8.9 Hz, 4H), 7.75 (d, $J$ = 8.9 Hz, 2H), 7.84 (d, $J$ = 8.9 Hz, 4H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 27.7, 28.8, 29.1, 29.4, 31.7, 47.3, 47.7, 68.3, 83.9, 114.0, 114.5, 127.9, 129.0, 129.7, 130.0, 131.05, 131.10, 150.5, 162.2, 162.8. IR (neat) $\nu$/cm$^{-1}$: 2923, 2854, 1729, 1596, 1357, 1259, 1158. Anal. Calc. for $C_{84}H_{141}N_3O_{13}S_3$ (1497.25 g mol$^{-1}$): C 67.39, H 9.49, N 2.81, S 6.42; Found: C 67.31, H 9.39, N 2.78, S 6.14%.

**(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris{[3,4-di-(dodecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 7b.** This compound was obtained in the same way as **7a**. Silica gel chromatography was performed with hexanes–ethyl acetate (9.7 : 0.3). Yield 54%. Colourless oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.89 (t, $J$ = 6.6 Hz, 18H), 1.20–1.55 (complex absorption, 108H), 1.35 (s, 18H), 1.84 (m, 12H), 3.82 (d, $J$ = 5.9 Hz, 4H), 4.02 (t, $J$ = 6.4 Hz, 6H), 4.05 (t, $J$ = 6.5 Hz, 6H), 4.36 (d, $J$ = 5.2 Hz, 4H), 5.60 (dt, $J$ = 15.4 and 6.1 Hz, 2H), 5.77 (dt, $J$ = 15.4 and 5.6 Hz, 2H), 6.92 (d, $J$ = 8.6 Hz, 1H), 6.93 (d, $J$ = 8.6 Hz, 2H), 7.36 (d, $J$ = 2.2 Hz, 1H), 7.39 (d, $J$ = 2.2 Hz, 2H), 7.44 (dd, $J$ = 8.6 and 2.2 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.66, 25.69, 27.6, 28.7, 28.8, 28.9, 29.1, 29.2, 29.3, 29.4, 31.6, 47.4, 47.7, 68.86, 68.91, 69.2, 69.3, 83.7, 111.6, 112.2, 112.7, 120.6, 121.6, 127.9, 129.8, 131.1, 131.2, 148.1, 148.8, 150.4, 152.4, 153.0. IR (neat) $\nu$/cm$^{-1}$: 2921, 2852, 1728, 1587, 1260, 1136, 718. Anal. Calc. for $C_{108}H_{189}N_3O_{16}S_3$ (1881.89 g mol$^{-1}$): C 68.93, H 10.12, N 2.23, S 5.11; Found: C 68.89, H 9.86, N 2.19, S 4.99%.

**(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris{[3,4-di(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 7c.** This compound was obtained in the same way as **7a**. Silica gel chromatography was performed with hexanes–ethyl acetate (9.9 : 0.1). Yield 19%. Mp 47 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 18H), 1.20–1.60 (complex absorption, 156H), 1.43 (s, 18H), 1.84 (m, 12H), 3.83 (d, $J$ = 6.1 Hz, 4H), 4.03 (t, $J$ = 6.5 Hz, 6H), 4.06 (t, $J$ = 6.6 Hz, 6H), 4.36 (d, $J$ = 5.2 Hz, 4H), 5.61 (dt, $J$ = 15.4 and 6.1 Hz, 2H), 5.78 (dt, $J$ = 15.4 and 5.5 Hz, 2H), 6.93 (d, $J$ = 8.5 Hz, 1H), 6.94 (d, $J$ = 8.5 Hz, 2H), 7.36 (d, $J$ = 2.2 Hz, 1H), 7.39 (d, $J$ = 2.2 Hz, 2H), 7.45 (dd, $J$ = 8.5 and 2.2 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.70, 25.74, 27.6, 28.76, 28.84, 28.9, 29.0, 29.09, 29.12, 29.2, 29.39, 29.44, 31.7, 47.4, 47.8, 68.9, 69.0, 69.3, 69.4, 83.8, 111.7, 112.3, 112.8, 120.7, 121.6, 128.0, 129.8, 131.2, 131.3, 148.2, 148.8, 150.5, 152.4, 153.1. IR (neat) $\nu$/cm$^{-1}$: 2915, 2849, 1727, 1262, 1136. Anal. Calc. for $C_{132}H_{237}N_3O_{16}S_3$ (2218.53 g mol$^{-1}$): C 71.46, H 10.77, N 1.89, S 4.34; Found: C 71.32, H 11.22, N 1.81, S 3.63%.

**(*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris{[2,3,4-tri-(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 7d.** This compound was obtained in the same way as **7a**, using mixtures of acetonitrile–tetrahydrofuran (9 : 1) as solvents. Silica gel chromatography was performed with hexanes–diethyl ether (9.5 : 0.5). Yield 81%. Mp 30–33 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.6 Hz, 27H), 1.20–1.60 (complex absorption, 252H), 1.80 (m, 18H), 3.95 (apparent t, $J$ = 6.6 Hz, 8H), 4.03 (apparent t, $J$ = 5.8 Hz, 8H), 4.18 (complex absorption, 6H), 4.39 (apparent d, $J$ = 4.9 Hz, 4H), 5.65 (dt, $J$ = 15.2 and 6.1 Hz, 2H), 5.80 (dt, $J$ = 15.1 and 5.4 Hz, 2H), 6.67 (d, $J$ = 9.0 Hz, 1H), 6.68 (d, $J$ = 9.0 Hz, 2H), 7.58 (d, $J$ = 9.0 Hz, 1H), 7.68 (d, $J$ = 9.0 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.56, 25.62, 25.8, 25.9, 26.0, 27.6, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.45, 29.48, 29.9, 30.0, 30.3, 31.7, 47.48, 47.53, 47.9, 48.0, 68.8, 73.6, 74.5, 74.6, 83.1, 106.0, 125.4, 126.5, 126.7, 127.8, 130.2, 141.3, 142.3, 150.5, 151.0, 151.2, 157.0, 157.7. IR (neat) $\nu$/cm$^{-1}$: 2916, 2849, 1725, 1580, 1467, 1137, 1087. Anal. Calc. for $C_{180}H_{333}N_3O_{19}S_3$ (2939.82 g mol$^{-1}$): C 73.54, H 11.42, N 1.43, S 3.27; Found: C 73.39, H 11.40, N 1.41, S 3.15%.

### Synthesis of (*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazaundeca-3,8-dienes 1a–d

**(*E*,*E*)-1,6,11-Tris{[4-(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 1a. General procedure.** Trifluoroacetic acid (10 mL) was added to a solution of **7a** (0.57 g, 0.38 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 4 h and evaporated to dryness. The residue was partitioned between dichloromethane and water. The organic layer was dried with anhydrous $Na_2SO_4$ and evaporated to afford practically pure **1a** (0.45 g, 91% yield) as a white solid. A sample for elemental analysis was purified by digestion in $CHCl_3$–hexanes (1 : 1). Mp 109–111 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 9H), 1.18–1.57 (complex absorption, 78H), 1.79 (m, 6H), 3.50 (br m, 4H), 3.69 (d, $J$ = 6.8 Hz, 4H), 4.02 (t, $J$ = 6.5 Hz, 4H), 4.04 (t, $J$ = 6.4 Hz, 2H), 4.83 (br t, $J$ = 6.8 Hz, 2H, NH), 5.56 (br m, 4H), 6.97 (d, $J$ = 8.9 Hz, 6H), 7.70 (d, $J$ = 8.9 Hz, 2H), 7.79 (d, $J$ = 8.9 Hz, 4H). $^{13}$C NMR (62.5 MHz, $CDCl_3$, 54 °C): $\delta$ 14.4, 23.0, 26.3, 29.5, 29.67, 29.7, 29.90, 29.93, 30.0, 32.3, 44.7, 49.4, 69.0, 115.17, 115.20, 128.8, 129.6, 129.7, 130.1, 131.7, 131.8, 163.1. IR (neat) $\nu$/cm$^{-1}$: 3301, 3275, 2918, 2851, 1599, 1329, 1156. Anal. Calc. for $C_{74}H_{125}N_3O_9S_3$ (1297.01 g mol$^{-1}$):

 

C 68.53, H 9.71, N 3.24, S 7.42; Found: C 67.92, H 9.69, N 3.24, S 7.05%.

**(*E*,*E*)-1,6,11-Tris{[3,4-di(dodecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 1b.** This compound was obtained in the same way as **1a**. Compound **1b** was purified by silica gel chromatography with hexanes–ethyl acetate (8 : 2). Yield 89%. Mp 80–82 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 18H), 1.20–1.65 (complex absorption, 108H), 1.83 (m, 12H), 3.51 (m, 4H), 3.69 (m, 4H), 4.03 (complex absorption, 12H), 4.91 (t, $J$ = 6.4 Hz, 2H, NH), 5.60 (br s, 4H), 6.92 (d, $J$ = 8.4 Hz, 2H), 6.94 (d, $J$ = 8.4 Hz, 1H), 7.25 (d, $J$ = 2.0 Hz, 1H), 7.35 (dd, $J$ = 8.4 and 2.0 Hz, 1H), 7.36 (d, $J$ = 2.0 Hz, 2H), 7.45 (dd, $J$ = 8.4 and 2.0 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 28.8, 28.9, 29.08, 29.11, 29.14, 29.34, 29.37, 29.4, 31.7, 44.0, 49.2, 69.0, 69.2, 69.4, 111.2, 111.9, 112.0, 120.6, 120.7, 128.1, 129.4, 130.5, 130.8, 148.7, 148.9, 152.5, 152.6. IR (neat) $\nu$/cm$^{-1}$: 3287, 3272, 2916, 2849, 1587, 1133. Anal. Calc. for $C_{98}H_{173}N_3O_{12}S_3$ (1681.66 g mol$^{-1}$): C 70.00, H 10.37, N 2.50, S 5.72; Found: C 70.20, H 10.30, N 2.48, S 5.73%.

**(*E*,*E*)-1,6,11-Tris{[3,4-di(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 1c.** This compound was obtained in the same way as **1a** (yield 99% from **7c**). Compound **1c** was also obtained from **6c**, following the general procedure as for **7a**, using sodium hydride (10 eq.) as a base and dimethylformamide as a solvent. During this process, allylation of sulfonamide **1c** and deprotection of Boc groups of the resulting product **7c** occurred at the same time (47% yield of **1c** from **6c**). Mp 66–68 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 18H), 1.20–1.60 (complex absorption, 156H), 1.83 (m, 12H), 3.52 (m, 4H), 3.69 (m, 4H), 4.02 (complex absorption, 12H), 4.83 (t, $J$ = 9.7 Hz, 2H, NH), 5.61 (br s, 4H), 6.92 (d, $J$ = 8.4 Hz, 1H), 6.94 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 2.0 Hz, 1H), 7.34 (dd, $J$ = 8.4 and 2.0 Hz, 1H), 7.35 (d, $J$ = 2.0 Hz, 2H), 7.44 (dd, $J$ = 8.4 and 2.0 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 28.8, 28.9, 21.10, 29.14, 29.2, 29.37, 29.40, 29.45, 31.7, 44.0, 49.2, 69.0, 69.3, 69.5, 111.3, 112.0, 112.1, 120.6, 120.7, 128.2, 129.4, 130.5, 130.9, 148.7, 149.0, 152.6, 152.7. IR (neat) $\nu$/cm$^{-1}$: 3278, 2916, 2849, 1263, 1136. Anal. Calc. for $C_{122}H_{221}N_3O_{12}S_3$ (2018.30 g mol$^{-1}$): C 72.60, H 11.04, N 2.08, S 4.77; Found: C 72.59, H 11.08, N 2.04, S 4.27%.

**(*E*,*E*)-1,6,11-Tris{[2,3,4-tri(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazaundeca-3,8-diene, 1d.** This compound was obtained in the same way as **1a**. Compound **1d** was purified by silica gel chromatography with hexanes–diethyl ether (9 : 1). Yield 74%. Mp 45–47 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.88 (t, $J$ = 6.5 Hz, 27H), 1.20–1.60 (complex absorption, 234H), 1.83 (m, 18H), 3.39 (m, 4H), 3.74 (m, 4H), 4.00 (complex absorption, 12H), 4.19 (complex absorption, 6H), 4.85 (t, $J$ = 6.3 Hz, 2H, NH), 5.48 (br s, 4H), 6.66 (d, $J$ = 9.1 Hz, 1H), 6.69 (d, $J$ = 9.1 Hz, 2H), 7.52 (d, $J$ = 9.1 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.6, 25.85, 25.9, 26.0, 28.9, 29.12, 29.15, 29.20, 29.23, 29.29, 29.36, 29.42, 29.45, 29.48, 29.53, 29.88, 30.1, 31.3, 31.7, 44.6, 48.0, 68.8, 73.52, 73.53, 74.7, 74.9, 106.5, 106.8, 124.4, 124.7, 125.4, 126.1, 128.2, 129.1, 141.9, 142.4, 150.2, 151.1, 157.2, 157.4. IR (neat) $\nu$/cm$^{-1}$: 3270, 2916, 2849, 1580, 1467, 1087. Anal. Calc. for $C_{170}H_{317}N_3O_{15}S_3$ (2739.58 g mol$^{-1}$): C 74.53, H 11.66, N 1.53, S 3.51; Found: C 74.43, H 12.13, N 1.38, S 3.15%.

### Synthesis of (*E*,*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes 2a–d

**(*E*,*E*,*E*)-1,6,11-Tris{[4-(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene, 2a. General procedure.** A solution of **1a** (0.50 g, 0.39 mmol) and 1,4-dibromo-2-butene (0.085 g, 0.39 mmol) in acetonitrile–THF (25 : 50 mL) was added dropwise over 3 h to a stirred suspension of anhydrous potassium carbonate (0.27 g, 1.93 mmol) in boiling acetonitrile–THF (25 : 50 mL). The mixture was heated under reflux for 20 h, the salts were filtered off, and the filtrate was evaporated. The residue was purified by column chromatography on silica gel with hexanes–THF (9.5 : 0.5) to afford **2a** (0.13g, 25% yield) as a white solid. Mp 87–88 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 7.2 Hz, 9H), 1.20–1.50 (complex absorption, 78H), 1.83 (m, 6H), 3.69 (br s, 12H), 4.03 (t, $J$ = 6.4 Hz, 6H), 5.60 (br s, 6H), 6.99 (d, $J$ = 8.8 Hz, 6H), 7.71 (d, $J$ = 8.8 Hz, 6H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.5, 23.1, 26.4, 29.5, 29.8, 29.96, 30.00, 30.06, 30.09, 30.7, 32.3, 51.1, 68.9, 115.20, 125.9, 129.7, 129.9, 130.8, 136.2, 163.0. IR (neat) $\nu$/cm$^{-1}$: 2922, 2852, 1596, 1336, 1256, 1154. Anal. Calc. for $C_{78}H_{129}N_3O_9S_3$ (1349.09 g mol$^{-1}$): C 69.44, H 9.64, N 3.11, S 7.13; Found: C 69.13, H 9.98, N 3.06, S 6.91%.

**(*E*,*E*,*E*)-1,6,11-Tris{[3,4-di(dodecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene, 2b.** This compound was obtained in the same way as **2a**. Compound **2b** was purified by silica gel chromatography with hexanes–diethyl ether (9 : 1). Yield 68%. Mp 45–46 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 18H), 1.20–1.56 (complex absorption, 108H), 1.84 (m, 12H), 3.69 (br s, 12H), 4.02 (t, $J$ = 6.6 Hz, 6H), 4.05 (t, $J$ = 6.6 Hz, 6H), 5.63 (s, 6H), 6.93 (d, $J$ = 8.4 Hz, 3H), 7.24 (d, $J$ = 2.2 Hz, 3H), 7.34 (dd, $J$ = 8.4 and 2.2 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.7, 28.8, 28.9, 29.10, 29.13, 29.33, 29.36, 29.40, 31.6, 50.5, 69.0, 69.4, 111.7, 112.1, 120.7, 129.3, 130.0, 148.8, 152.6. IR (neat) $\nu$/cm$^{-1}$: 2917, 2849, 1586, 1260, 1139. Anal. Calc. for $C_{102}H_{177}N_3O_{12}S_3$ (1733.73 g mol$^{-1}$): C 70.66, H 10.29, N 2.42, S 5.55; Found: C 70.55, H 10.26, N 2.35, S 5.28%.

**(*E*,*E*,*E*)-1,6,11-Tris{[3,4-di(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene, 2c.** This compound was obtained in the same way as **2a**. Compound **2c** was purified by silica gel chromatography with hexanes–diethyl ether (9 : 1). Yield 61%. Mp 78–80 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.6 Hz, 18H), 1.20–1.60 (complex absorption, 156H), 1.86 (m, 12H), 3.68 (br s, 12H), 4.03 (t, $J$ = 6.6 Hz, 6H), 4.06 (t, $J$ = 6.6 Hz, 6H), 5.63 (br s, 6H), 6.94 (d, $J$ = 8.5 Hz, 3H), 7.24 (d, $J$ = 2.2 Hz, 3H), 7.34 (dd, $J$ = 8.5 and 2.2 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.5, 23.1, 26.4, 29.5, 29.6, 29.77, 29.81, 29.85, 30.05, 30.08, 30.13, 32.3, 51.2, 69.7, 70.0, 112.2, 112.7, 121.4, 129.96, 130.6, 149.5, 153.3. IR (neat) $\nu$/cm$^{-1}$: 2916, 2849, 1266, 1135. MALDI-TOF-MS ($m/z$): 2091.6 (M + Na)$^+$, 2107.5 (M + K)$^+$. Anal. Calc. for

$C_{126}H_{225}N_3O_{12}S_3$ (2070.37 g mol$^{-1}$): C 73.10, H 10.95, N 2.03, S 4.65; Found: C 73.13, H 10.97, N 2.24, S 4.31%.

**(*E*,*E*,*E*)-1,6,11-Tris{[2,3,4-tri(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-triene, 2d.** This compound was obtained in the same way as **2a**. Compound **2d** was purified by silica gel chromatography with hexanes–diethyl ether (9 : 1). Yield 82%. Mp 43–44 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.5 Hz, 27H), 1.20–1.60 (complex absorption, 234H), 1.84 (m, 18H), 3.78 (br s, 12H), 3.99 (t, $J$ = 6.5 Hz, 6H), 4.02 (t, $J$ = 6.3 Hz, 6H), 4.16 (t, $J$ = 7.0 Hz, 6H), 5.67 (br s, 6H), 6.65 (d, $J$ = 9.0 Hz, 3H), 7.55 (d, $J$ = 9.0 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.6, 25.85, 25.94, 29.0, 29.11, 29.16, 29.3, 29.5, 30.0, 30.2, 31.7, 50.4, 68.7, 73.5, 74.7, 106.5, 125.1, 125.8, 129.7, 142.4, 151.1, 157.2. IR (neat) $\nu$/cm$^{-1}$: 2916, 2849, 1579, 1467, 1088. MALDI-TOF-MS (*m*/*z*): 2812.3 $(M + Na)^+$, 2828.3 $(M + K)^+$. Anal. Calc. for $C_{174}H_{321}N_3O_{15}S_3$ (2791.66 g mol$^{-1}$): C 74.86, H 11.59, N 1.51, S 3.45; Found: C 74.26, H 12.12, N 1.51, S 3.30%.

### Synthesis of (*E*,*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienespalladium(0), 3a–d

**(*E*,*E*,*E*)-1,6,11-Tris{[4-(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), 3a. General procedure.** A solution of macrocycle **2a** (0.047 g, 0.035 mmol) and tetrakis(triphenylphosphane)palladium(0) (0.048 g, 0.042 mmol) in tetrahydrofuran (5 mL) was heated under reflux for 24 h. The solvent was evaporated and the residue was purified by silica gel chromatography with hexanes–ethyl acetate (9 : 1) to afford **3a** (0.015 g, 30% yield) as a white solid. Mp 153 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.4 Hz, 9H), 1.20–1.50 (complex absorption, 78H), 1.70–1.90 (complex absorption, 10H), 2.84 (apparent t, $J$ = 12.0 Hz, 2H), 3.10 (dd, $J$ = 13.7 and 11.0 Hz, 2H), 3.77 (apparent d, $J$ = 8.7 Hz, 2H), 3.99 (t, $J$ = 6.4 Hz, 6H), 4.03 (m, 2H), 4.66 (apparent d, $J$ = 13.9 Hz, 4H), 4.80 (br d, $J$ = 13.2 Hz, 2H), 6.95 (d, $J$ = 8.9 Hz, 4H), 6.96 (d, $J$ = 9.1 Hz, 2H), 7.69 (d, $J$ = 8.9 Hz, 4H), 7.77 (d, $J$ = 9.1 Hz, 2H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.5, 23.1, 26.4, 29.43, 29.47, 29.8, 29.95, 29.99, 32.3, 45.6, 48.7, 49.9, 68.9, 78.9, 79.2, 83.3, 115.2, 129.5, 129.6, 130.0, 130.9, 136.5, 162.89, 162.98. IR (neat) $\nu$/cm$^{-1}$: 2922, 2851, 1596, 1338, 1258, 1157, 419. MALDI-TOF-MS (*m*/*z*): 1453.2 $(M)^+$, 1476.3 $(M + Na)^+$, 1370.8 $(M - Pd + Na)^+$, 1386.4 $(M - Pd + K)^+$. Anal. Calc. for $C_{78}H_{129}N_3O_9PdS_3$ (1455.51 g mol$^{-1}$): C 64.34, H 8.93, N 2.89, S 6.61; Found: C 64.27, H 9.19, N 2.80, S 6.46%.

**(*E*,*E*,*E*)-1,6,11-Tris{[3,4-di(dodecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), 3b.** This compound was obtained in the same way as **3a**. Yield 97%. Mp 70–71 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 18H), 1.20–1.58 (complex absorption, 108H), 1.64–1.90 (complex absorption, 16H), 2.82 (apparent t, $J$ = 11.9 Hz, 2H), 3.10 (apparent dd, $J$ = 13.8 and 11.2 Hz, 2H), 3.76 (m, 2H), 4.00 (m, 14H), 4.62 (m, 4H), 4.78 (d, $J$ = 13.7 Hz, 2H), 6.89 (d, $J$ = 8.6 Hz, 2H), 6.90 (d, $J$ = 8.6 Hz, 1H), 7.21 (d, $J$ = 2.2 Hz, 2H), 7.28 (d, $J$ = 2.2 Hz, 1H), 7.32 (dd, $J$ = 8.6 and 2.2 Hz, 2H), 7.40 (dd, $J$ = 8.6 and 2.2 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.68, 25.72, 28.75, 28.78, 28.9, 29.1, 29.2, 29.33, 29.37, 29.42, 31.6, 44.9, 48.0, 49.2, 68.9, 69.4, 78.3, 78.5, 82.6, 111.5, 111.6, 111.98, 112.01, 120.4, 120.6, 129.4, 130.1, 148.7, 148.8, 152.5, 152.6. IR (neat) $\nu$/cm$^{-1}$: 2920, 2850, 1585, 1261, 1152, 902. Anal. Calc. for $C_{102}H_{177}N_3O_{12}PdS_3$ (1840,15 g mol$^{-1}$): C 66.58, H 9.69, N 2.28, S 5.23; Found: C 66.21, H 9.51, N 2.20, S 5.17%.

**(*E*,*E*,*E*)-1,6,11-Tris{[3,4-di(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), 3c.** This compound was obtained in the same way as **2a**, using Pd(dibenzylideneacetone)$_2$, [Pd(dba)$_2$], as the palladium(0) source. Compound **2d** was purified by silica gel chromatography with hexanes–ethyl acetate (9.5 : 0.5). Yield 54%. Mp 72–74 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 6.6 Hz, 18H), 1.20–1.60 (complex absorption, 156H), 1.60–1.70 (complex absorption, 4H), 1.85 (m, 12H), 2.83 (apparent t, $J$ = 11.5 Hz, 2H), 3.11 (apparent dd, $J$ = 14.5 and 11.1 Hz, 2H), 3.78 (br d, $J$ = 10.6 Hz, 2H), 4.01 (m, 14H), 4.61 (br d, $J$ = 10.0 Hz, 2H), 4.65 (br d, $J$ = 13.6 Hz, 2H), 4.78 (br d, $J$ = 12.5 Hz, 2H), 6.89 (d, $J$ = 8.6 Hz, 3H), 7.21 (d, $J$ = 2.2 Hz, 2H), 7.23 (d, $J$ = 2.2 Hz, 1H), 7.33 (dd, $J$ = 8.6 and 2.2 Hz, 2H), 7.40 (dd, $J$ = 8.6 and 2.2 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 14.4, 23.3, 26.4, 29.43, 29.47, 29.6, 29.80, 29.82, 29.85, 30.05, 30.08, 30.10, 30.13, 32.03, 44.8, 48.2, 49.3, 68.6, 70.0, 78.4, 78.6, 83.1, 111.3, 111.4, 111.9, 112.2, 120.9, 121.2, 129.96, 130.03, 130.76, 148.5, 148.6, 153.3, 153.4. IR (neat) $\nu$/cm$^{-1}$: 2916, 1849, 1262, 1137. MALDI-TOF-MS (*m*/*z*): 2197.5 $(M + Na)^+$, 2213.5 $(M + K)^+$. Anal. Calc. for $C_{126}H_{225}N_3O_{12}PdS_3$ (2176.79 g mol$^{-1}$): C 69.52, H 10.42, N 1.93, S 4.42; Found: C 69.38, H 10.36, N 1.80, S 3.78%.

**(*E*,*E*,*E*)-1,6,11-Tris{[2,3,4-tri(hexadecyloxy)phenyl]sulfonyl}-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), 3d.** This compound was obtained in the same way as **3a**, using [Pd(dba)$_2$] as the palladium(0) source. Compound **3d** was purified by silica gel chromatography with hexanes–diethyl ether (9.5 : 0.5). Yield 27%. Mp 43–44 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 6.5 Hz, 27H), 1.20–1.55 (complex absorption, 234H), 1.65–2.00 (complex absorption, 22H), 3.12 (complex absorption, 4H), 3.89 (complex absorption, 2H), 3.94 (t, $J$ = 6.6 Hz, 6H), 4.02 (t, $J$ = 6.4 Hz, 6H), 4.12 (m, 2H), 4.16 (t, $J$ = 6.5 Hz, 6H), 4.64 (apparent t, $J$ = 14.7 Hz, 4H), 4.80 (d, $J$ = 13.0 Hz, 2H), 6.67 (d, $J$ = 8.9 Hz, 2H), 6.69 (d, $J$ = 8.5 Hz, 1H), 7.60 (d, $J$ = 8.9 Hz, 2H), 7.63 (d, $J$ = 8.5 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 13.8, 22.4, 25.6, 25.9, 28.89, 28.94, 29.11, 29.3, 29.40, 29.45, 29.51, 29.9, 30.1, 31.7, 44.8, 48.0, 49.2, 68.2, 73.3, 73.4, 74.8, 79.5, 83.5, 106.5, 125.0, 125.1, 125.4, 126.0, 126.9, 127.9, 128.6, 129.7, 130.3, 134.1, 141.3, 142.2, 142.3, 144.7, 151.1, 151.2, 157.1, 157.2. IR (neat) $\nu$/cm$^{-1}$: 2916, 2849, 1579, 1467, 1089. MALDI-TOF-MS (*m*/*z*): 2896.1 $(M + H)^+$, 2812.3 $(M - Pd + Na)^+$, 2828.3 $(M - Pd + K)^+$. $C_{174}H_{321}N_3O_{15}PdS_3$ (2898.08 g mol$^{-1}$).

### Techniques

Melting points were determined with a Kofler apparatus and are uncorrected. IR spectra were recorded with an FT-IR

 

spectrophotometer using a single-reflection ATR system as a sampling accessory. NMR spectra were recorded with a Bruker-Analytik AC250. $^1$H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at $\delta = 7.28$ and tetramethylsilane at $\delta = 0.00$. $^{13}$C NMR (62.5 MHz) are reported relative to $CHCl_3$ at $\delta = 77.0$ and tetramethylsilane at $\delta = 0.0$. MALDI-TOF spectra were recorded on a BIFLEX spectrometer (Brucker-Franzen Analityk) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using 19 kV acceleration voltage. Matrices (α-cyanocinnamic acid) were prepared at 5 mg $mL^{-1}$ in THF. Analytes were dissolved at a concentration between 0.1 and 5.0 ng $mL^{-1}$ in THF or chloroform. Elemental analyses were determined at ''Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona'' and ''Servei de Microanàlisi del CSIC de Barcelona''.

The textures of the mesophases were studied using an optical microscope (Olympus BH-2) with crossed polarisers and connected to a Linkam THMS600 hot stage and a Linkam TMS91 central processor. Microphotographs were taken with a DP12 Olympus camera, adapted to the microscope. Measurements of the transition temperatures were made using a TA2910 differential scanning calorimeter with a heating or cooling rate of 10 °C $min^{-1}$. The apparatus was calibrated with indium (156.6 °C, 28.44 J $g^{-1}$) and tin (232.1 °C, 60.5 J $g^{-1}$).

Powder X-ray diffraction patterns were obtained using a Pinhole (Anton–Paar) diffractometer and Ni-filtered Cu-Kα radiation. The samples were held in Lindemann glass capillaries ($\Phi = 1$ mm) and heated with a variable temperature attachment. The diffraction patterns were collected on photographic films.

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