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Wide temperature range mesomorphic behaviour of highly fluorinated 15-membered macrocycles and their open trisulphonamide precursor

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The mesomorphic properties of 15-membered azamacrocycles containing long hydrocarbon or highly fluorinated long chains have been explored along with those of their open precursors. The liquid crystalline behaviour is determined by the presence of different heteroatoms or long fluorinated chains and the substitution pattern of the aryl units of the sulphonamides. The presence of highly fluorinated long chains in the *para* position with regard to the sulphonamide group was found to favour the formation of smectic mesophases with wide temperature ranges. All of the mesophases were studied by polarizing optical microscopy and differential scanning calorimetry.

1. Introduction

Fluorinated materials have attracted a great deal of attention because of their unique properties [1]. The replacement of one or several hydrogen atoms by fluorine confers to the resulting materials peculiar properties such as special solubility, increase chemical and oxidative stability, decrease of flammability or increase melting point, which make them suitable for many applications, e.g. surface coatings, fire retardants, biomedicines, etc. The synthesis of highly fluorinated functional compounds and the use of these materials in the elaboration of molecular organized systems have received special attention [2]. Perfluorinated alkyl chains have attracted great interest in liquid crystal research during the last few years because of their ability to promote wide liquid crystal temperature ranges, chemical stability, reduced flexibility and the possibility of introducing additional dipole moments [3]. It is well known that the introduction of fluoro-substituents into a side chain enhances the smectic character of a liquid crystal [4]. Moreover, the introduction of fluoro-substituents within liquid crystal systems leads to materials that are of considerable technological interest [5] for display [6] or non-display (electronic industry) [7] applications.

In a previous paper we explored the mesomorphic properties of suitably designed triolefinic 15-membered azamacrocycles containing long alkoxy chains in the aromatic rings [8]. The presence of a hexadecyloxy chain in the *para* position of each benzene ring of the azamacrocycle promoted calamitic mesomorphic behaviour. In contrast, 3,4-dialkoxybenzenesulphonamide derivatives (C_{12} and C_{16}) led to molecules that show columnar mesomorphism. The presence of three endocyclic olefins is thought to increase the rigidity of the cycles and play an important role in the supramolecular arrangements of the molecules. In addition, these endocyclic double bonds have the ability to coordinate transition metals such as palladium(0), which also had a marked influence on the mesomorphic behaviour. Moreover, macrocycles and their corresponding Pd(0) complexes containing several highly fluorinated or polyoxyethylene chains on the aromatic rings are also able to stabilize Pd(0) nanoparticles [9]. Interestingly, liquid crystalline properties were also observed in open tris-benzenesulphonamide precursors of some of these macrocycles. The versatility in the preparation of this family of azamacrocycles, and the promising results obtained in the field of liquid crystals, prompted us to prepare new sulphonamide derivatives containing long highly fluorinated chains in an effort to obtain mesogenic compounds with wide mesophase temperature ranges. To the best of our knowledge, fluorinated macrocyclic liquid crystals have not been reported often in the literature. One example concerns amphiphilic molecules based on the calix[4]arene scaffold and these show smectic phases [10].

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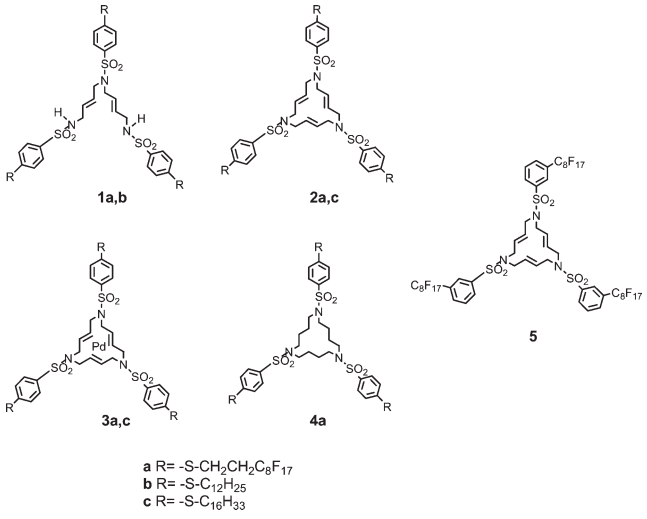

Figure 1. The 15-membered azamacrocycles studied in this work.

With these ideas in mind we designed a 15-membered triolefinic azamacrocycle incorporating long polyfluorinated alkylthio chains (**2a** in figure 1). The corresponding open precursor (**1a**), Pd(0) complex (**3a**) and the fully saturated derivative (**4a**) were also prepared in order to assess the influence of the flexibility of the central mesogenic part on the mesomorphic behaviour. The preparation of these compounds was readily achieved by following a new, simple methodology to prepare 4-substituted phenylsulphonamides by S_NAr reaction on weakly activated 4-fluorobenzenesulphonamides with several N, O and S nucleophiles, which was published recently [11]. A triple substitution of the fluorine atoms of (*E*,*E*,*E*)-1,6,11-tris[(4-fluorophenyl)-sulphonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene provided a new and easy way to obtain azamacrocycles bearing highly fluorinated chains attached through a sulphur atom in the *para* position of the arenesulphonamides. In order to establish the role of the fluoroalkylthio tails as either promoters or stabilizers of liquid crystalline behaviour, analogous hydrocarbon derivatives (**1b**, **2c** and **3c**) were also studied. Compound **5** [9] was prepared to study the influence of the position of the perfluorinated chains on the macrocycles as well as the presence or absence of heteroatoms in these tails.

2. Results and discussion

2.1. *Synthesis*

The synthesis of compounds **1**–**4** is outlined in figure 2. The key common step in the preparation of all the

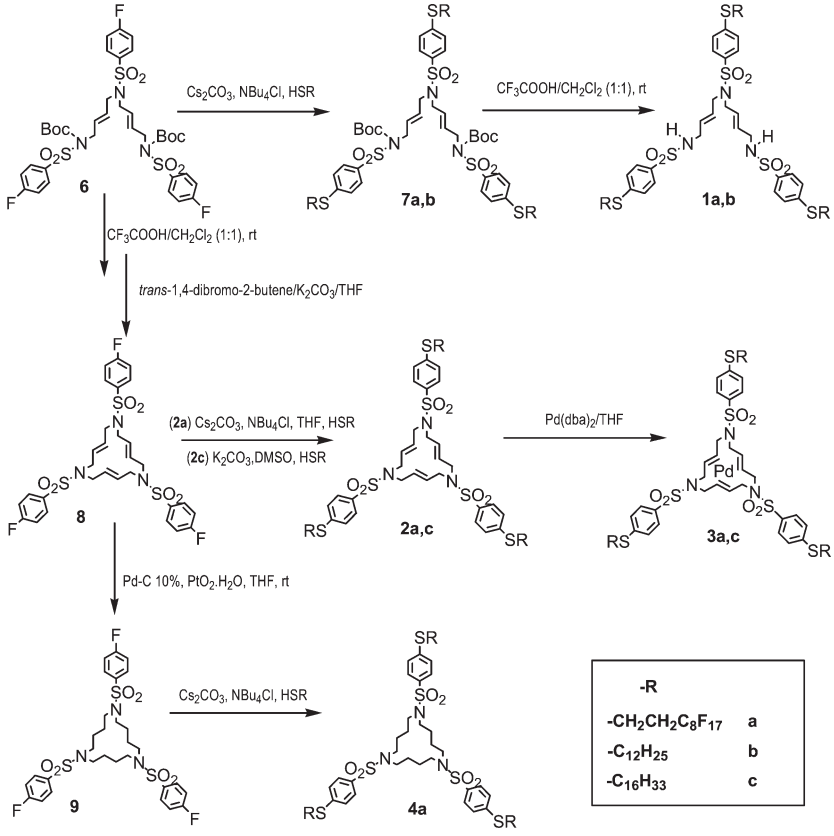

Figure 2. The synthesis of compounds **1**–**4**.

compounds described here is the nucleophilic substitution of a fluorine atom by an alkylthio tail according to procedures described elsewhere [11, 12], which mainly involve the use of Cs_2CO_3 and NBu_4Cl in anhydrous THF. In this way, the corresponding fluoro-derivative within each series, i.e. **6** [9], **8** [12] and **9** [9], enabled the preparation of the target molecules with either fluoroalkylthio or alkylthio terminal tails. Aromatic nucleophilic substitution of all three fluorine atoms of **6** with the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (series **a**) or dodecylthiol (series **b**) and subsequent cleavage of the Boc protecting groups with trifluoroacetic acid/dichloromethane (1:1) at room temperature, gave the open precursors **1a** and **1b**, respectively. Macrocycles **2a**,**c** [11] and **4a** [9] were prepared directly from **8** or its fully hydrogenated derivative **9**, respectively, by nucleophilic aromatic substitution of all three fluoro-substituents by the corresponding thiol. Palladium(0) complexes **3a**,**c** were prepared by metal exchange using Pd(dibenzylideneacetone)$_2$ (Pd(dba)$_2$) as the palladium(0) source in THF under reflux.

Compound **5**, which contains long perfluorinated chains in the *meta* position of each aromatic ring, was synthesised stepwise according to a previously described strategy from the corresponding commercially available 3-perfluorooctylbenzenesulphonamide and *trans*-1,4-dibromo-2-butene [9].

2.2. *Mesomorphic behaviour*

The thermal behaviour of the compounds reported here was studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The thermal data are given in table 1. X-ray diffraction experiments on the mesophases could not be carried out due to the low stability of the compounds at the corresponding temperatures during the prolonged periods of time necessary for irradiation.

The presence of a single partially fluorinated alkylthio tail in the *para* position of each benzene ring promotes mesomorphic behaviour in the azamacrocycles, both in the olefinic (**2a**) and saturated (**4a**) compounds as well as in the open precursor **1a**. The palladium(0) complex **3a** decomposes at 195°C. Curiously, POM and DSC studies gave results consistent with the thermal properties of the corresponding ligand **2a**, which indicates that the ligand separates from the palladium(0) centre at the temperature in question. It is reasonable to believe that the additional forces resulting from the metal-metal interactions in the complex increase the melting point and preclude the appearance of mesomorphic behaviour prior to decomplexation.

All three mesogenic compounds exhibited a SmA mesophase, which appeared with the natural texture shown in figure 3. As can be seen in the photomicrograph, all the compounds demonstrated a high tendency to adopt homeotropic alignment on cooling from the isotropic liquid between glass plates. This observation is probably due to the influence of the hydrophobic nature of the fluorinated terminal tails. In addition, small focal conic domains were also seen on cooling from the liquid.

Table 1. Thermal and thermodynamic properties measured during the second heating–cooling cycle. Temperatures are given in °C. Enthalpies are given in kJ mol^{-1} and appear in brackets.

Compound	Mesomorphic behaviour				
1a	C	167.7 (82)	SmA	225.0 (3.1)	I
1b	C	138			I
2a	C	183.2 (89)	SmA	216.6 (5.5)	I
2c	C	87 (40)			I
3a	C	195			Dec.
3c	C	100–120			Dec.
4a	C	166.6 (52.2)	SmA	204.1 (5.1)	I

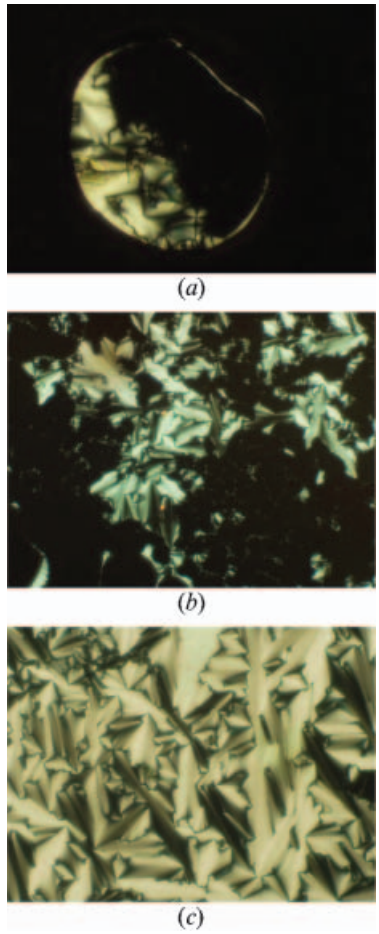

Figure 3. Polarized optical micrograph of the SmA mesophase of compounds (a) **1a** (180°C), (b) **2a** (190°C) and (c) **4a** (200°C) taken on cooling from the isotropic liquid.

The data in table 1 clearly show the strong stabilization achieved on incorporating fluorinated tails in this type of compound. It is worth mentioning that the presence of a sulphur atom as the linker between the hydrocarbon alkyl tails and the aromatic nucleus (**2c**) prevents the appearance of mesomorphic behaviour, a situation in contrast to the alkoxy derivative [8]. The high levels of fluorination in the terminal chains overcomes the negative effect of the presence of the thioether linkage and, as a result, not only compound **2a** but also **1a** and **4a** show mesomorphic behaviour, in contrast to **1b** and **2c**. Along with an increase in the melting temperatures, lateral intermolecular interactions are strongly conducive to lamellar organization, thus promoting the appearance of the SmA mesophase. In fact the incompatibility of the fluorocarbon chains with the hydrocarbon *N*-phenylsulphonyl-substituted triazamacrocycle leads to a microsegregation process, which has a marked influence on the molecular arrangement in the mesophase. Indeed, this microsegregation must account for the appearance and stabilization of the mesomorphic layered arrangement in which the molecules may well adopt a conformation in which the three 4-fluoroalkylthiophenyl groups lie parallel to one another in such a way that one of the branches is oriented to the opposite side with respect to the other two [13].

It should be noted at this point that macrocycle **5** – containing perfluoroalkyl tails in the *meta* position in the aromatic rings – does not show mesomorphic behaviour. It appears that it is not only the presence of perfluorinated chains in the macrocycles, but also the substitution pattern on the aromatic rings and the presence of heteroatoms that are responsible for the behaviour of the compounds as liquid crystals.

Another aspect that warrants attention is the effect that the nature (either saturated or nonsaturated) of the azamacrocycle has on transition temperatures. Hydrogenation of the macrocycle (compound **4a**) increases the flexibility of the central molecular moiety and this gives rise to a decrease in the melting and clearing temperatures. However, the mesophase range remains essentially unchanged with respect to the unsaturated analogue **2a** (figure 4, table 1). Nevertheless, the strongest tendency for mesomorphic behaviour corresponds to the open precursor **1a**, which, as well as having similar melting temperatures to **4a**, shows the highest clearing point. The presence of primary sulphonamide groups provides the opportunity for H-bonding interactions within the mesophase, a factor that would be expected to further stabilise the phase.

3. Conclusions

The presence of long highly fluorinated chains in the family of compounds reported here enhances the probability of obtaining liquid crystals in comparison to the hydrocarbon analogues. Triolefinic and fully hydrogenated 15-membered macrocycles containing three 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecylthio)benzenesulphonamide groups show mesomorphism. Smectic A mesophases are observed over wide temperature ranges. Open precursor **1a** shows enhanced liquid crystal stability, probably due to the presence of intermolecular hydrogen bonds. Macrocycle **5**, which contains perfluorinated tails in the *meta* position of each of the benzene rings, is not mesogenic. The nature of the heteroatom used to link the polyfluoroalkyl chains to the aromatic rings does not impede the appearance of mesomorphism, in contrast to the alkylthio analogue **2c**.

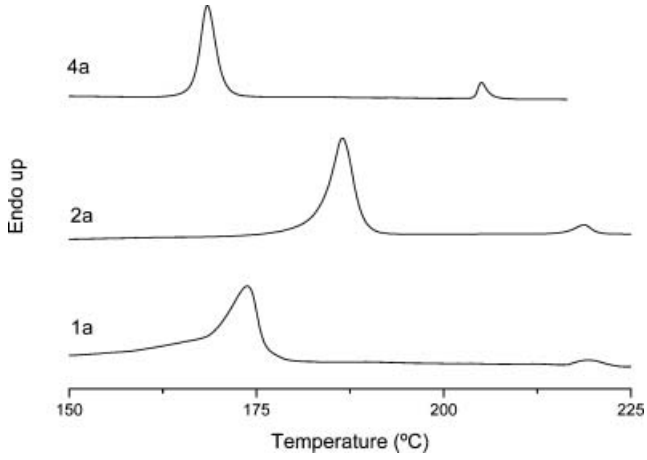

Figure 4. DSC scans corresponding to the second heating process at a rate of 10°C min^{-1}.

4. Experimental

4.1. *Synthesis*

The synthesis of compounds **2a**,**c**, **3a**, **4a**, **6**, **8** and **9** is described elsewhere [9, 11]. The synthesis of **7a**,**b**, **1a**,**b** and **3c** was carried out as follows.

4.1.1. (*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris-{[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl thio)phenyl]sulphonyl}-1,6,11-triazaundeca-3,8-diene, IVa. 1*H*,1*H*,2*H*,2*H*-Perfluorodecanethiol (2.41 g, 5.03 mmol) was added dropwise during 20 min under an inert atmosphere to a stirred suspension of Cs_2CO_3 (2.64 g, 8.09 mmol) and NBu_4Cl (0.23 g, 0.81 mmol) in anhydrous THF (6 ml). The mixture was stirred for 30 min and a solution of (*E*,*E*)-1,11-bis(*tert*-butyloxycarbonyl)-1,6,11-tris[(4-fluorophenyl)sulphonyl]-1,6,11-triazaundeca-3,8-diene (**I**) (0.67 g, 0.81 mmol) in anhydrous THF (6 ml) was slowly added. The mixture was stirred for 48 h at room temperature. The salts were filtered off and the filtrate was evaporated to dryness. The residue

was chromatographed on silica gel with hexanes/ethyl acetate (97/3) to afford **IVa** (0.44 g, 25% yield) as a low melting solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35 (s, 18H), 2.46 (m, 6H), 3.24 (m, 6H), 3.87 (d, J=5.7 Hz, 4H), 4.40 (d, J=5.4 Hz, 4H), 5.63 (dt, J=15.3 and 6.2 Hz, 2H), 5.80 (dt, J=15.3 and 5.5 Hz, 2H), 7.40 (d, J=8.6 Hz, 6H), 7.77 (d, J=8.6 Hz, 2H), 7.84 (d, J=8.6 Hz, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 23.5 (bs), 28.2, 30.1, 31.6 (tt, J=88.7 and 19.2 Hz), 48.0, 48.4, 85.1, 127.3, 127.9, 128.3, 128.4, 129.1, 130.4, 137.7, 138.0, 142.1, 143.1, 150.9. ^{19}F NMR (235.2 MHz, $CDCl_3$): δ −126.7, −123.9, −123.3, −122.5, −114.8, −113.5, −106.0. IR (neat) ν/cm^{-1}: 1727, 1581, 1360, 1202, 1142, 708. MALDI-TOF-MS (m/z) calculated for $C_{66}H_{54}F_{51}N_3O_{10}S_6$: 2232.1 (M+Na$^+$), 2248.1 (M+K$^+$). Found: 2233.5 (M+Na$^+$), 2248.5 (M+K$^+$).

4.1.2. (*E*,*E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris-{[4-(dodecylthio)phenyl]sulphonyl}-1,6,11-triazaundeca-3,8-diene, IVb. Dodecanethiol (0.60 g, 2.98 mmol) was added dropwise during 20 min under an inert atmosphere to a stirred suspension of Cs_2CO_3 (1.29 g, 3.97 mmol), NBu_4Cl (0.014 g, 0.05 mmol) in anhydrous THF (8 ml). The mixture was stirred for 30 min and a solution of (*E*,*E*)-1,11-bis(*tert*-butyloxycarbonyl)-1,6,11-tris[(4-fluorophenyl)sulphonyl]-1,6,11-triazaundeca-3,8-diene (**I**) (0.41 g, 0.50 mmol) in anhydrous THF (8 ml) was slowly added. The mixture was stirred for 36 h at room temperature. The salts were filtered off and the filtrate was evaporated to dryness. The residue was chromatographed through silica gel with hexanes/ethyl acetate (97:3) to afford **IVb** (0.21 g, 31% yield) as a colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.89 (t, J=6.6 Hz, 9H), 1.24–1.55 (complex absorption, 54H), 1.35 (s, 18H), 1.68 (m, 6H), 2.99 (t, J=7.4 Hz, 6H), 3.83 (d, J=5.9 Hz, 4H), 4.38 (d, J=5.4 Hz, 4H), 5.61 (dt, J=15.4 and 6.1 Hz, 2H), 5.78 (dt, J=15.4 and 5.6 Hz, 2H), 7.34 (d, J=8.6 Hz, 6H), 7.70 (d, J=8.6 Hz, 2H), 7.77 (d, J=8.6 Hz, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.5, 23.1, 28.3, 29.0, 29.1, 29.3, 29.4, 29.6, 29.7, 29.88, 29.93, 29.98, 30.03, 32.3, 32.4, 32.5, 48.0, 48.4, 84.9, 126.5, 127.2, 127.9, 128.5, 128.7, 130.4, 136.2, 136.5, 145.1, 146.2, 151.0. IR (neat) ν/cm^{-1}: 2923, 2851, 1728, 1359, 1162, 1100, 1073, 760, 640. MALDI-TOF-MS (m/z) calculated for $C_{72}H_{117}N_3O_{10}S_6$: 1398.6 (M+Na$^+$), 1414.6 (M+K$^+$). Found: 1398.2 (M+Na)$^+$, 1414.2 (M+K$^+$).

4.1.3. (*E*,*E*)-1,6,11-Tris{[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecylthio)phenyl]sulphonyl}-1,6,11-triazaundeca-3,8-diene, 1a. General procedure. Trifluoroacetic acid (7 ml) was added to a solution of **IVa** (0.17 g, 0.12 mmol) in dichloromethane (7 ml). The mixture was stirred at room temperature for 6 h and evaporated to dryness. The residue was dissolved in dichloromethane and the solution was washed twice with aqueous $NaHCO_3$ and once more with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was washed with ether/pentane (9:1) and dried. Yield 89% (0.084 g) as a yellow solid, mp 178–179°C. ^{1}H NMR (250 MHz, THF-D_8, 323 K): δ 2.44–2.72 (complex absorption, 6H), 3.30 (m, 6H), 3.46 (t, J=5.2 Hz, 4H), 3.66 (d, J=5.5 Hz, 4H), 5.71 (m, 4H), 6.53 (bt, J=6.0 Hz, 2H, NH), 7.45 (d, J=8.3 Hz, 4H), 7.46 (d, J=8.2 Hz, 2H), 7.71 (d, J=8.2 Hz, 2H), 7.74 (d, J=8.3 Hz, 4H). ^{13}C NMR (62.5 MHz, THF-D_8, 323 K): δ 24.1 (hidden carbon signals behind THF-D_8 signals), 30.4, 32.1 (t, J=85.8 Hz), 45.0, 49.1, 128.2, 128.5, 128.6, 128.8, 131.7, 138.2, 138.5, 140.4, 142.1. ^{19}F NMR (235.2 MHz, THF-D_8, 323 K): δ −128.9, −125.9, −125.4, −124.5, −116.6. IR (neat) ν/cm^{-1}: 3307, 3280, 1582, 1328, 1199, 1146, 710. MALDI-TOF-MS (m/z) calculated for $C_{56}H_{38}F_{51}N_3O_6S_6$: 2009.0 (M$^+$), 2032.0 (M+Na$^+$), 2048.0 (M+K$^+$). Found: 2010.2 (M$^+$), 2032.2 (M+Na$^+$), 2048.2 (M+K$^+$).

4.1.4. (*E*,*E*)-1,6,11-Tris{[4-(dodecylthio)phenyl]sulphonyl}-1,6,11-triazaundeca-3,8-diene, 1b. This product was obtained by the same procedure as **1a**. Product **1b** was isolated (0.13 g, 89% yield) as a white solid, mp 133–134°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.90 (t, J=6.6 Hz, 9H), 1.24–1.54 (complex absorption, 54H), 1.69 (m, 6H), 3.00 (m, 6H), 3.51 (m, 4H), 3.68 (d, J=4.1 Hz, 4H), 5.08 (t, J=6.2 Hz, 2H, NH), 5.56 (m, 4H), 7.33 (d, J=8.7 Hz, 4H), 7.34 (d, J=8.7 Hz, 2H), 7.65 (d, J=8.7 Hz, 2H), 7.74 (d, J=8.7 Hz, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.5, 23.1, 29.0, 29.3, 29.6, 29.8, 29.9, 30.0, 30.04, 30.06, 32.3, 32.5, 44.7, 49.6, 126.98, 127.05, 127.82, 127.91, 128.6, 130.1, 135.8, 136.1, 145.4. IR (neat) ν/cm^{-1}: 2918, 2849, 1326, 1158, 1102, 852. MALDI-TOF-MS (m/z) calculated for $C_{62}H_{101}N_3O_6S_6$: 1198.6 (M+Na$^+$), 1214.6 (M+K$^+$). Found: 1200.4 (M+Na$^+$), 1216.0 (M+K$^+$).

4.1.5. (*E*,*E*,*E*)-1,6,11-Tris{[4-(hexadecylthio)phenyl]sulphonyl}-1,6,11-triazacyclopenta deca-3,8,13-trienepalladium(0), 3c. A solution of macrocycle **2c** (0.40 g, 0.29 mmol) and Pd(dibenzylideneacetone)$_2$ (0.20 g, 0.34 mmol) in THF (10 ml) was heated under reflux overnight. The solvent was evaporated and the residue was purified by silica gel chromatography with hexanes/ethyl acetate (increasing polarity) to afford **3c** (0.30 g, 70% yield) as a grey solid, mp (decomposition) 100–120 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.90 (t, J=6.5 Hz, 9H), 1.18–1.53 (complex absorption, 78H), 1.63–1.80 (complex absorption, 10H),

2.84 (t, J=12.8 Hz, 2H), 2.98 (t, J=7.3 Hz, 6H), 3.13 (dd, J=14.0 and 11.1 Hz, 2H), 3.77 (d, J=8.5 Hz, 2H), 4.00 (m, 2H), 4.66 (d, J=13.9 Hz, 4H), 4.80 (d, J=13.9 Hz, 2H), 7.31 (d, J=8.5 Hz, 4H), 7.32 (d, J=8.5 Hz, 2H), 7.64 (d, J=8.5 Hz, 4H), 7.71 (d, J=8.5 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.8, 22.4, 28.4, 28.6, 28.9, 29.1, 29.2, 29.4, 31.7, 31.8, 44.9, 48.0, 49.2, 78.3, 78.5, 82.6, 126.4, 127.1, 134.0, 134.8, 144.6, 144.9. IR (neat) ν/cm^{-1}: 2920, 2850, 1338, 1161. Analysis calculated for $C_{78}H_{129}N_3O_6PdS_6$ (1503.7 g mol^{-1}): C 62.31, H 8.65, N 2.79, S 12.79; found: C 62.05, H 8.64, N 2.68, S 12.51.

4.2. *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 δ=7.28 and tetramethylsilane at δ=0.00 and to THF at δ=1.72 and 3.58. ^{13}C NMR (62.5 MHz) are reported relative to $CHCl_3$ at δ=77.0 and tetramethylsilane at δ=0.0 and to THF at δ=25.3 and 67.4. ^{19}F NMR (235.2 MHz) are reported relative to trichlorofluoromethane at δ=0.00. MALDI-TOF spectra were recorded on a BIFLEX spectrometer (Bruker-Franzen Analityk) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using 19 kV acceleration voltage. Matrices (2,5-dihydroxybenzoic acid) were prepared at 5 mg ml^{-1} in THF. Analytes were dissolved at a concentration between 0.1 and 5.0 μg ml^{-1} in THF or chloroform. Elemental analyses were carried out at ''Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona''.

The textures of the mesophases were studied using an optical microscope (Olympus BH-2) with crossed polarizers in conjunction with a Linkam THMS600 hot stage and a Linkam TMS91 central processor. Microphotographs were taken with a DP12 Olympus camera, adapted to the microscope. The transition temperatures were determined 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}).

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