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Mesomorphic silver(I) complexes of 4-alkyloxy-2′-stilbazoles and 4-alkyloxy-3′-stilbazoles. Crystal and molecular structure of 4-methoxy-2′-stilbazole†

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Three new series of silver(I) complexes $[AgL_2][X]$ have been synthesised and their mesomorphism has been established. The new compounds were obtained by the complexation of 4-alkyloxy-3′-stilbazole and 4-alkyloxy-2′-stilbazole ligands, respectively, to silver(I) dodecyl sulfate (DOS), and to silver(I) triflate (OTf). Thus, they differ from previously reported 4-alkyloxy-4′-stilbazole silver complexes in that the new stilbazole ligands are isomers by virtue of having the 4-alkyloxystyryl group attached to the pyridine ring in the 2- or 3-position. The complexes are mesomorphic, displaying only a smectic A phase providing that a sufficient number of carbon atoms are present in the terminal aliphatic chain. The thermal behaviour observed for the new isomeric series is compared and discussed on the basis of simple structural arguments which account for the differences in mesomorphism and stability.

Introduction

In recent years, numerous studies of mesomorphic metal complexes of alkyloxystilbazoles‡ have been carried out[1] and the chemistry of ionic complexes of 4-alkyloxy-4′-stilbazoles with silver(I) is well developed.[2] The structure of these complexes is shown in Fig. 1 (**1a–e**) and derivatives have been synthesised with a wide variety of anions, X^-, such as BF_4^- (**1a**), NO_3^- (**1b**), triflate (OTf^-, **1c**) and alkyl sulfate (*e.g.* $C_8H_{17}OSO_3^-$ (OS^-, **1d**); $C_{12}H_{25}OSO_3^-$ (DOS^-, **1e**)). With the anions BF_4^-, NO_3^- or OTf^-, the complexes showed mainly SmA and SmC phases, with a nematic phase being observed for the short chain-length silver triflates. Clearing temperatures were usually high (>240 °C) and decomposition occurred close to, or at, the clearing point. However, for the OS^- and DOS^- salts, clearing temperatures were often much lower (*ca.* 180 °C) as were the melting points. The complexes showed nematic, SmA and SmC phases, but the DOS^- derivatives differed from the others as they also displayed a cubic phase, between the SmC and SmA phases, when the alkyloxy chains possessed more than six carbon atoms.

Recently, the synthesis of 4-alkyloxy-2′-stilbazoles (**2**) and of 4-alkyloxy-3′-stilbazoles (**3**) (Fig. 2) was reported.[3] Concurrently, we had begun the synthesis of the same ligands with a view to undertaking a study of their complexes with silver(I), which are related to those we had studied previously. Thus, so far in silver complexes of this type, the influence of anion type,[2] anion chain length[4] and the number of alkyloxy chains attached to the ligand[5] have been studied, while the influence of the core structure and geometry, a possibility offered by these stilbazoles, has not yet been investigated. The preparation of these new complexes (Fig. 3) with DOS^- and OTf^- as counter-anion was therefore undertaken and the results of the investigation of their thermal behaviour are now presented.

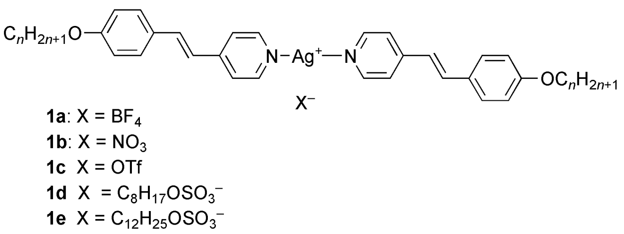

Fig. 1 Structure of the 'parent' silver(I) complexes of 4-stilbazoles.

Results

Synthesis

The syntheses employed for the 4-alkyloxy-3′-stilbazole and 4-alkyloxy-2′-stilbazole ligands differ from those reported recently.[3] Thus, 4-alkyloxy-2′-stilbazoles (**2**) were prepared using a Heck[6] methodology by reacting 4-alkyloxy(iodo)benzene (itself prepared in a Williamson ether reaction from 4-iodophenol and a 1-bromoalkane) with 2-vinylpyridine and a

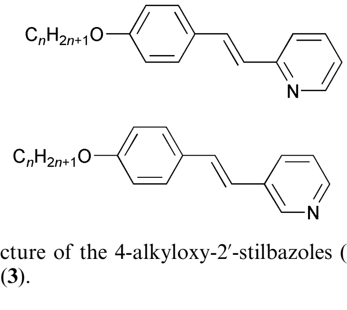

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Fig. 2 Structure of the 4-alkyloxy-2′-stilbazoles (**2**) and 4-alkyloxy-3′-stilbazoles (**3**).

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†Electronic supplementary information (ESI) available: bond lengths and angles for 4-methoxy-2′-stilbazole. See http://www.rsc.org/suppdata/jm/b2/b204820e/

‡The IUPAC name for stilbazole is (2-phenylvinyl)pyridine.

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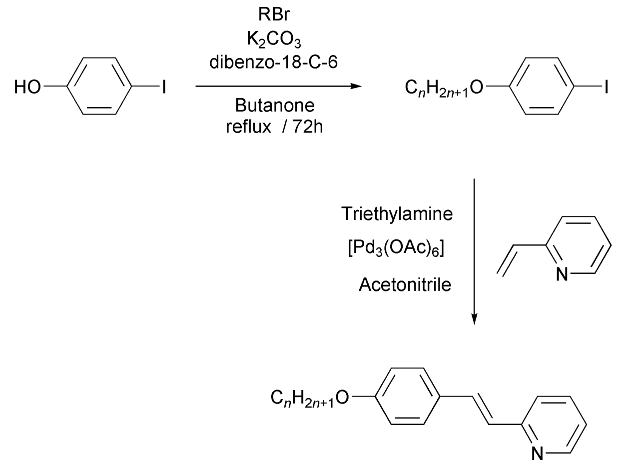


Scheme 1 Synthesis of the 4-alkyloxy-2′-stilbazoles. *Reagents and conditions*: i) $C_nH_{2n+1}Br$, K_2CO_3, dibenzo-18-crown-6, butanone, reflux 72 h; ii) 2-vinylpyridine, MeCN, Et_3N, $[Pd_3(OAc)_6]$ (cat.), 100 °C, 96 h, constant volume.

palladium catalyst (Scheme 1). The reaction was carried out in acetonitrile in a thick-walled Fisher–Porter vessel at 100 °C for 96 h at constant volume giving yields of up to 86%. This method was used previously for the synthesis of 4-alkyloxy-4′-stilbazoles.[7]

The preparation of the 4-alkyloxy-3′-stilbazoles (**3**) differed as 3-vinylpyridine is not available commercially. Thus, 4-acetoxystyrene was reacted with 3-bromopyridine in the presence of triethylamine and Herrmann's catalyst.[8] The reaction was carried out in acetonitrile in a thick-walled Fisher–Porter vessel at 100 °C for 96 h at constant volume, giving a yield of 70%. The acetoxystilbazole so produced was then deprotected with alcoholic potassium hydroxide under reflux giving 4-hydroxy-3′-stilbazole. Treated with the appropriate 1-bromoalkane in the presence of caesium carbonate in DMF (room temperature for 24 h), the required 4-alkyloxy-3′-stilbazoles were obtained in reasonable yields (Scheme 2).

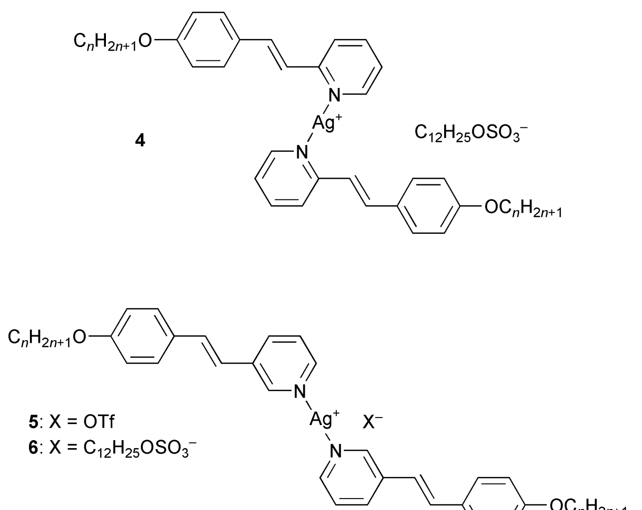


Fig. 3 Structure of the new silver(I) complexes.

The silver(I) dodecyl sulfate complexes of both ligand types (**4** and **6**) were prepared by stirring the appropriate stilbazole with silver(I) dodecyl sulfate in CH_2Cl_2 at room temperature for 15 h protected from light.

Only 4-alkyloxy-3′-stilbazole complexes of silver triflate (**5**) were prepared as complexation of 4-alkyloxy-2′-stilbazoles was unsuccessful. The appropriate 4-alkyloxy-3′-stilbazole was stirred in acetone with silver(I) triflate for 4 h at room temperature protected from light and, after cooling in ice, the product was recovered by filtration.

Crystal and molecular structure of 4-methoxy-2′-stilbazole

In order to obtain a greater degree of structural information, single crystals of 4-methoxy-2′-stilbazole were grown from petroleum ether (b.p. 40–60) and a structure determined, which is depicted with its atomic numbering scheme in Fig. 4. Crystallographic data are collected in Table 1, while bond lengths and angles are given in the ESI.

The molecular structure consists of two essentially planar moieties (Fig. 5)—a 4-methoxyphenylethene group (C1, O1, C2 > C7, C8, C9) with only methyl hydrogens situated out of the plane, which is bonded in a *trans* configuration to 2-pyridine (C10, N1, C11 > C14). These two planar fragments form a dihedral angle of 14.08(10)° with respect to each other.

There are no classical hydrogen bonds observed in the structure, however it packs as corrugated zig-zag sheets, propagating in the *ab* plane of the unit cell. Each molecule packs in a head-to-tail fashion with those above and below it. $\pi\cdots\pi$ Separations of 4.062(4) and 5.009(5) Å exist between the pyridine and methoxy substituted rings above and below the plane of the molecule, respectively (Fig. 6).

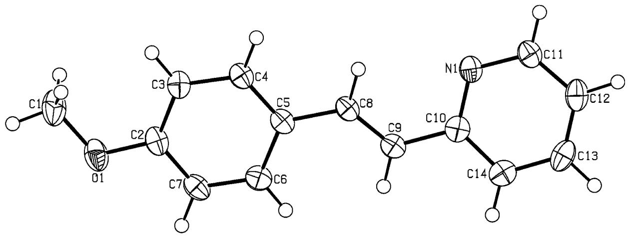
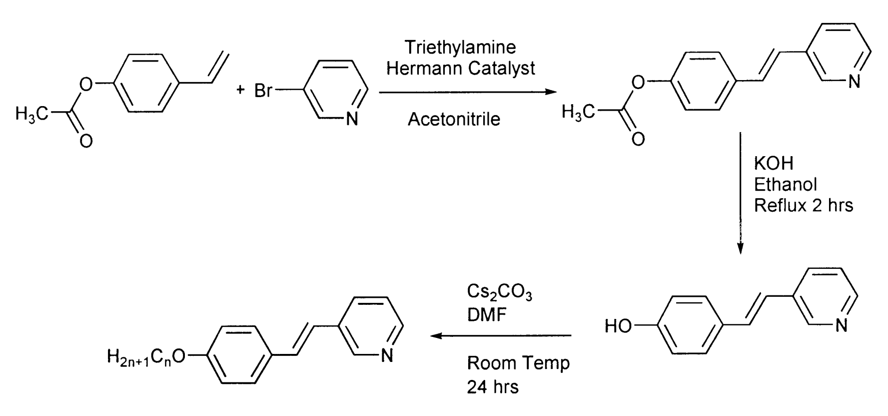


Fig. 4 Molecular structure of 4-methoxy-2′-stilbazole.



Scheme 2 Synthesis of the 4-alkyloxy-3′-stilbazoles. *Reagents and conditions*: i) Et_3N, Herrmann's catalyst, MeCN, 96 h, 100 °C, constant volume; ii) KOH, EtOH, reflux 2 h; iii) $C_nH_{2n+1}Br$, Cs_2CO_3, DMF, rt, 24 h.

Table 1 Crystal data and structure refinement parameters

Empirical formula	$C_{14}H_{13}NO$
Formula weight	211.25
Temperature/K	150(2)
Wavelength/Å	0.71073
Crystal system	Orthorhombic
Space group	*Iba*2
Unit cell dimensions	a = 9.2463(18) Å α = 90° b = 33.461(7) Å β = 90° c = 7.2285(14) Å γ = 90°
Volume/Å^3	2236.4(8)
Z	8
Density (calculated)/Mg m^{-3}	1.255
Absorption coefficient/mm^{-1}	0.079
F(000)	896
Crystal	Plate; colourless
Crystal size/mm^3	0.60 × 0.30 × 0.08
θ range for data collection/°	3.65–27.49
Index ranges	$-11 \leqslant h \leqslant 11$, $-41 \leqslant k \leqslant 43$, $-8 \leqslant l \leqslant 9$
Reflections collected	7063
Independent reflections	2481 [R_{int} = 0.0717]
Completeness to θ = 27.49°	99.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9937 and 0.9541
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2481/1/147
Goodness-of-fit on F^2	1.022
Final R indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.0576, wR_2 = 0.1372
R indices (all data)	R_1 = 0.0722, wR_2 = 0.1471
Absolute structure parameter	0.1(19)
Extinction coefficient	0.029(5)
Largest diff. Peak and hole	0.209 and −0.273 e Å^{-3}

Table 2 Thermal data for the new complexes

Complex	n	Transition	T/°C	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
4	4	Cr→I	114.7	46.2	119
	5	Cr→I	180.5	48.7	107
	6	Cr→I	87.4	39.6	110
		(SmA→I)	(80.5)	(−4.8)	(−14)
	7	Cr→SmA	78.5	15.6	44
		SmA→I	84.4	0.3	1
	8	Cr_1→Cr_2	41.4	4.4	14
		Cr_2→SmA	86.9	45.1	125
		SmA→I	94.2	2.9	8
	12	Cr_1→Cr_2	44.9	10.2	32
		Cr_2→SmA	79.4	23.8	68
		SmA→I	109.7	4.2	11
5	4	Cr→I	182.7	40.1	88
	8	Cr→I	154.2	53.2	125
		(SmA→I)	(144.8)	(−5.8)	(−14)
	12	Cr→SmA	142.0	56.1	135
		SmA→I	174.5	5.2	12
6	4	Cr_1→Cr_2	85.2	9.9	28
		Cr_2→I	154.2	50.1	117
	8	Cr_1→Cr_2	66.4	1.9	6
		Cr_2→Cr_3	80.9	6.5	18
		Cr_3→SmA	146.2	49.7	119
		SmA→I	150.4	6.4	15
	12	Cr_1→Cr_2	55.5	0.5	2
		Cr_2→Cr_3	65.0	2.7	8
		Cr_3→SmA	139.0	45.1	110
		SmA→I	154.5	4.6	11

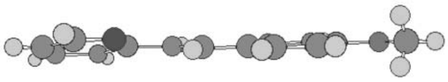


Fig. 5 Side-on view of 4-methoxy-2′-stilbazole.

Mesomorphism

The mesomorphism was studied by polarised optical microscopy, differential scanning calorimetry and X-ray diffraction. The complete mesomorphism of the complexes bis(4-alkyloxy-2′-stilbazole)silver(I) dodecyl sulfate (**4**), bis(4-alkyloxy-3′-stilbazole)silver(I) dodecyl sulfate (**6**) and bis(4-alkyloxy-3′-stilbazole)silver(I) triflate (**5**) is reported in Table 2 and is summarised in Figs. 7 and 8. Previous studies[3] of some of these materials reported the observation of ordered smectic phases on cooling from the isotropic melt. In contrast, in our hands, none of these stilbazoles was mesomorphic. However, on complexation of the non-mesomorphic ligands to the different silver salts, mesomorphic materials resulted providing that a sufficient number of carbon atoms were present in the terminal aliphatic chain. The complexes (**4**–**6**) displayed only one type of mesophase, namely the SmA mesophase, which was recognised on the basis of its optical textures, namely, a typical oily streak texture was seen during heating, and bâtonnets formed on cooling from the isotropic liquid.

For the DOS$^-$ salts of the 2-stilbazoles (**4**), the shortest-chain homologues examined (n = 4, 5) were non-mesomorphic and the SmA phase first appeared monotropically for the hexyloxy derivative, becoming enantiotropic thereafter. For the related complexes of 3-stilbazoles (**6**), the butyloxy derivative was non-mesomorphic, but an enantiotropic SmA phase was seen for both the octyloxy and dodecyloxy derivatives. The derivative with n = 8 showed a mesomorphic range of 4 K increasing to around 16 K for the n = 12 derivative. Finally, the triflate complexes (**5**) showed a monotropic SmA phase for the

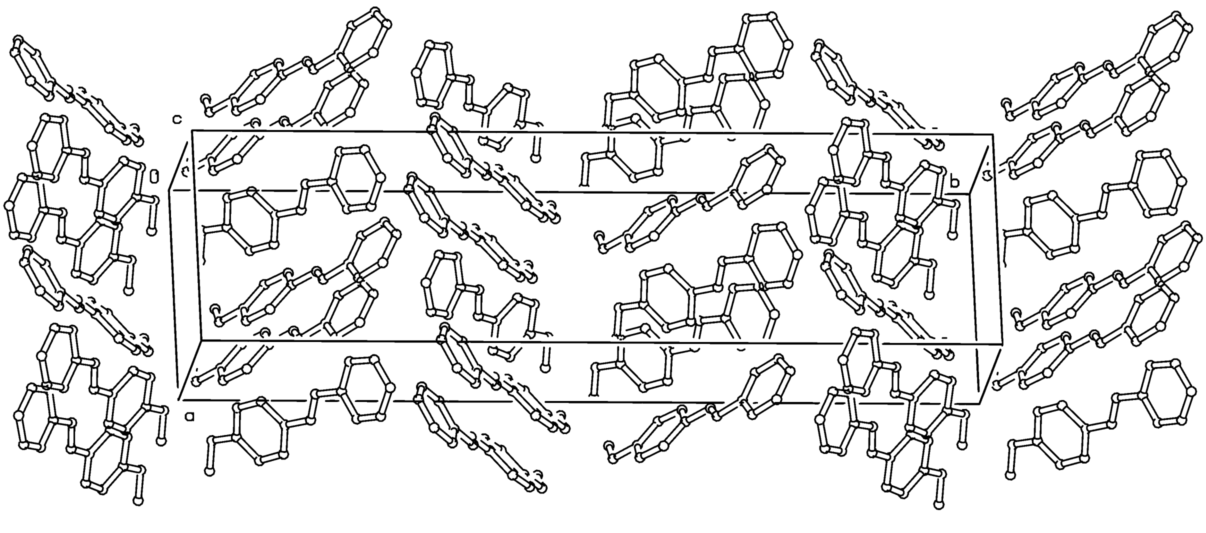


Fig. 6 Packing diagram for 4-methoxy-2′-stilbazole.

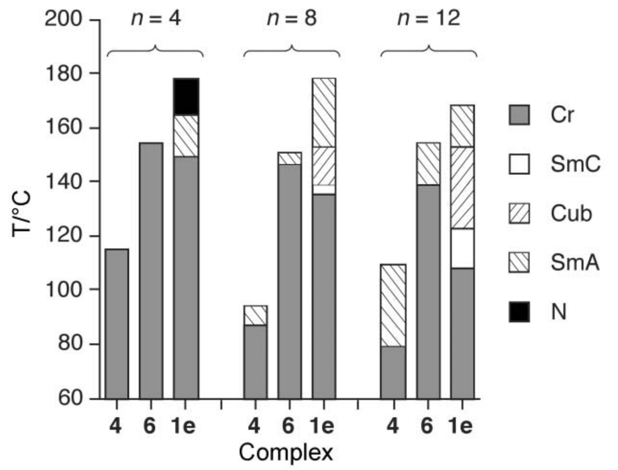


Fig. 7 Comparison of the thermal behaviour of the new silver(I) DOS complexes (**4** and **6**) with their 'parent' complexes (**1e**).

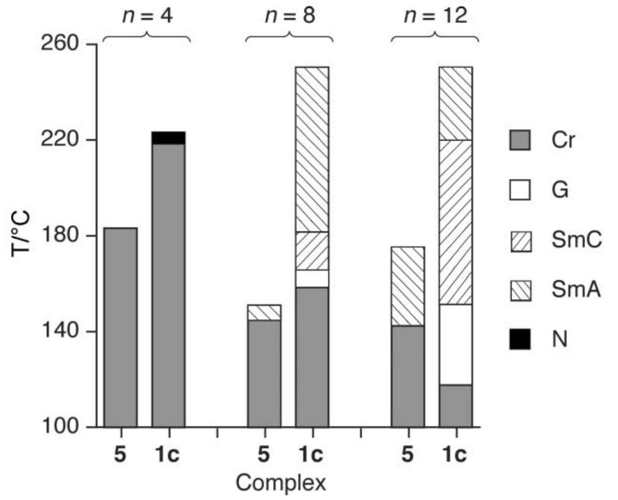


Fig. 8 Comparison of the thermal behaviour of the new silver(I) OTf complexes (**5**) with their 'parent' complexes (**1c**).

octyloxy derivative, becoming enantiotropic for a dodecyloxy chain.

X-Ray diffraction studies

In order to confirm the smectic nature of the mesophases, and to gain more insight into the molecular organisation within the SmA phase of the new complexes, X-ray diffraction experiments were undertaken. For **4** ($n = 12$), the X-ray pattern, recorded at 90 °C, showed two sharp, equidistant, small-angle reflections corresponding to the first and second orders of diffraction, respectively ($d_{001} = 34.2$ Å, $d_{002} = 17.2$ Å), consistent with a layered structure. In addition, an intense but diffuse scattering at *ca.* 10.0 Å and a diffuse halo at 4.6 Å were also observed. The latter corresponds to the liquid-like order of the alkyloxy chains, while the former may correspond to loose interactions within the layer between dimeric species formed by the silver complexes as suggested previously.[9,10] A similar pattern was recorded for **6** ($n = 12$) at 142 °C ($d_{001} = 37.2$ Å, $d_{002} = 18.7$ Å and broad peaks at 9.9 Å and 4.6 Å) and for **5** ($n = 12$) at 150 °C ($d_{001} = 42.6$ Å, $d_{002} = 21.2$ Å and two broad halos at 10.0 Å and 4.6 Å). All these results are consistent with a lamellar mesophase and, along with the optical textures, confirm the SmA phase type. The periodicity of **1** ($X^- = DOS^-$, $n = 12$), measured previously ($d_{001} = 43.6$ Å),[11] is given here for comparison.

As might have been expected, the periodicity of the SmA layers formed by these silver dodecyl sulfate salts (**1**: 43.6 Å, **4**: 34.2 Å, **6**: 37.2 Å) decrease with the decrease in molecular anisotropy in the order **1** > **6** > **4**. For **1**, the calculated length of the complex, in the most extended crystalline conformation, is 55.4 Å. The value of the SmA periodicity of **1** therefore reveals some combination of chain-coiling, chain-interdigitation and random, in-layer molecular tilt. The calculated length of complexes **4** and **6**, in the most extended crystalline conformation, have been estimated to be 48.4 Å and 53.8 Å respectively, leading to the same conclusions as in **1**. However, an interesting comparison is that of d_{001} for **6** ($n = 12$) and for **5** ($n = 12$), the former being 37.2 Å, while the latter is 42.6 Å. This is curious as the data represent the same mesogenic unit in terms of both ligand and chain length and yet there is a significant difference in *d* spacing. For complexes of 4-alkyloxy-4'-stilbazoles, a similar comparison was not possible for while such data were collected for the DOS^- salts, the SmA phase of the triflates was at rather high temperatures and decomposition precluded taking such measurements. At the present time, no clear explanation for this difference can be given.

The apparent molecular area, A_M, which represents the projection of the molecule onto the layer plane, was calculated directly from the molecular volume V_M[12] according to $A_M = V_M/d_{001}$. The values of A_M were found to increase from **1** (38 Å^2) to **6** (44 Å^2) to **4** (47 Å^2). These larger apparent molecular areas for **6** and **4**, which correspond to nearly twice what might be expected[13] for a classical calamitic mesogen in the SmA phase (*i.e.* 22–24 Å^2) are compatible with the reduced anisotropy of the complexes, as suggested earlier.

Attempts to represent the possible packing modes of these complexes are not straightforward, but one explanation for how they are arranged considers an idealised packing for **6**, as shown in Fig. 9. Here, space is filled by the anion chains aligning themselves along the rigid core of the cation (as found in the single crystal structure of an octyl sulfate complex of a 4-stilbazole[14]) and by interdigitation. Such a pronounced interdigitation would explain the fact that d_{001} was much smaller than expected and, if the smaller size of the triflate anion is taken into account, would explain why the observed d_{001} for **5** is much closer to the calculated length as the driving force for interdigitation would be largely removed.

However, where **4** is concerned the problem is very much more acute and simply bringing two complexes together as indicated in Fig. 10 illustrates well the problems of determining how they might pack.

The intense reflection at *ca.* 10 Å, observed for the new compounds, is an interesting feature of the XRD patterns. It is felt likely that this indicates the presence of dimeric complexes in the mesophase, and that the distance corresponds to the average distance between two such species. Let us remember that the crystalline structure of a silver(I) octyl sulfate complex consists of a dimeric structure, resulting from two parallel monomeric molecules where two silver cations are bridged by the sulfate groups.[13] Moreover, the crystal structure of a related silver(I) perchlorate complex with two pyridine fragments has been solved recently,[15] and showed a similar dimeric structure to the complex described above. In addition, we have recently obtained a further single crystal X-ray structure of a silver(I) alkyl sulfate complex and have, once more, found a similar motif.[16] Therefore, the presence of the scattering at 10 Å is compatible with the presence of dimeric species, and corresponds to the interdimeric distance given that such a structure remains unchanged in the mesophase.

Discussion

In looking at the mesomorphism of these new complexes, it is instructive to make comparison with the 'parent' complexes of

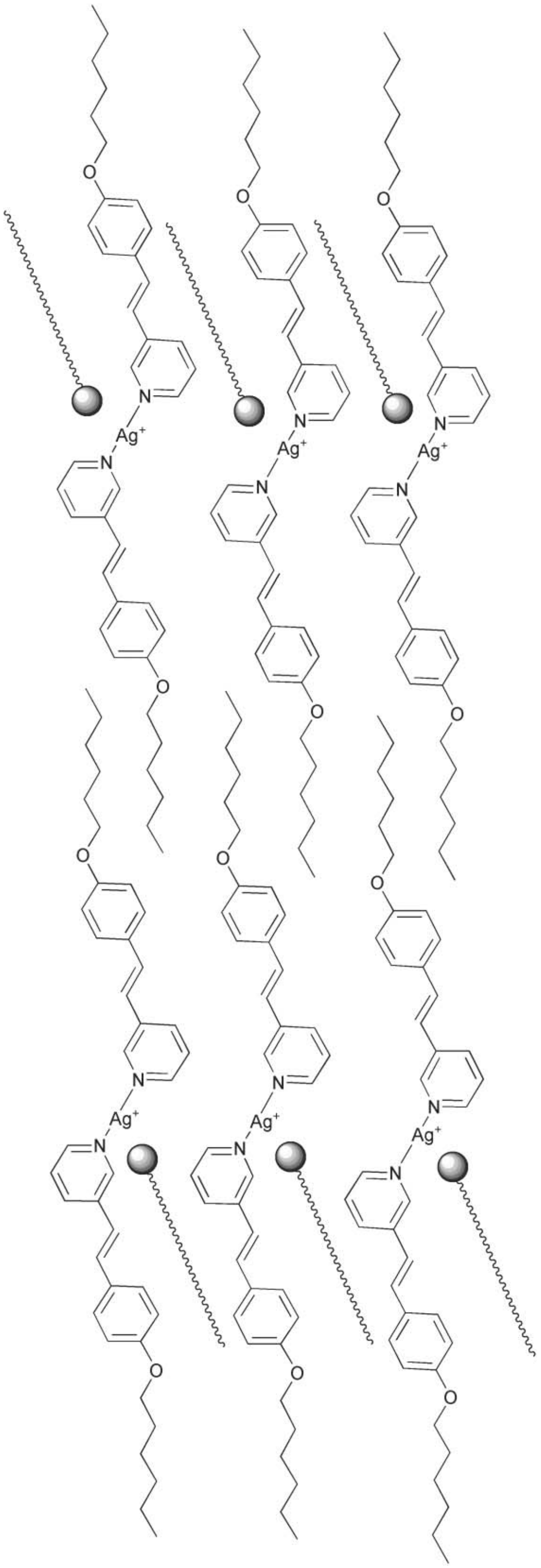


Fig. 9 Possible packing motif of the AgDOS complexes of the 4-alkyloxy-3′-stilbazoles.

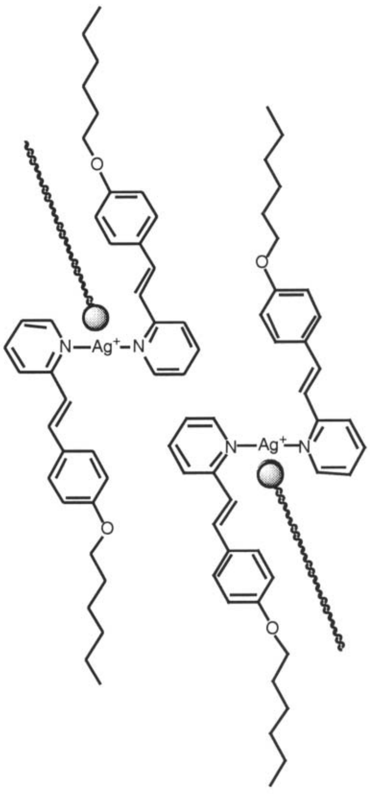


Fig. 10 Illustrative diagram to illustrate the difficulty in packing the AgDOS complexes of the 4-alkyloxy-2′-stilbazoles.

4-alkyloxy-4′-stilbazoles with both DOS$^-$ and OTf$^-$[17] anions. Thus, the complexes of the 4-alkyloxy-4′-stilbazoles clearly possess the most anisotropic structure of those being considered, followed by complexes of the 3-stilbazoles and then the 2-stilbazoles. Let us also recall that the replacement of the OTf$^-$ anion by the DOS$^-$ anion tends to destabilise the crystal phase and mesophases due to the introduction of a flexible, lateral substituent. Therefore, the higher transition temperatures found for the silver triflate complexes of the 4-alkyloxy-3′-stilbazoles (**5**) when compared with their DOS$^-$ analogues (**6**) and the fact that these temperatures are lower when compared to those found in the complexes of the 4-alkyloxy-4′-stilbazole parents can be understood by simple structural arguments. In a similar way, the transition temperatures of the AgDOS complexes of the 3-stilbazoles (**6**) are higher than those of the 2-stilbazoles (**4**) due to the greater molecular anisotropy in the former.

Consideration of the thermal behaviour in a little more detail reveals other valuable comparisons. Thus, the greatly reduced anisotropy of complexes **4** compared to **1**, leads to significant destabilisation of the crystal phase as well as the mesophase, whereas in **6**, this destabilisation is very much less (Fig. 7). For example, **6** ($n = 12$) melts at 139 °C and clears at 154.5 °C, **1** (X = DOS$^-$, $n = 12$) melts at 108 °C and clears at 168 °C, while **4** ($n = 12$) melts at 79.4 °C and clears at 109.7 °C. The destablisation of the SmA phase of **6** is modest at 14 °C, whereas it would appear that its crystal phase is stabilised. However, the fact that all of these new complexes show only a SmA phase does not allow such a ready comparison with the melting point of the parent systems where the first-formed fluid phase is a SmC phase. Comparison of **5** and **6** also reveals a much smaller destabilisation of the SmA phase on replacement of OTf$^-$ by DOS$^-$ (20 K for $n = 12$ and *ca.* 6 K for $n = 8$) than is the case for **1** where the value is typically some 70–80 °C.

Of course, the most dramatic comparison is made when simply considering the mesomorphism of the new materials against that of the parent complexes. Thus, complexes **1** are highly polymorphic whereas **4**–**6** all show only the SmA phase; the reason for this is not entirely clear. However, an important point is that for **4** and **6**, which formally possess a flexible, lateral chain, there is no nematic phase which would otherwise have been expected for a calamitic mesogen possessing such a chain.[18] This points to the rôle, in these systems, of intermolecular electrostatic interactions consequent on the presence of the silver cation and alkyl sulfate anion, a factor invoked previously to explain the mesomorphism of complexes of this type.[2,9,19] This also provides some clues concerning the molecular organisation in the mesophase as clearly, the packing must allow for the invoked cation–anion associations.

Experimental

All solvents and chemicals were used as received apart from THF which was further purified by distillation over sodium and benzophenone, dichloromethane which was distilled over calcium hydride, and acetone which was distilled over calcium sulfate, all under an atmosphere of oxygen-free nitrogen. Herrmann's catalyst was prepared according to literature procedures.[8]

NMR spectra were recorded on either a Bruker DFX 400 or ACF 300 spectrometer, operating at 400, or 300 MHz respectively for proton NMR. Elemental analyses were obtained from the School of Chemistry at the University of Exeter and from the Institut Charles Sadron, Strasbourg (microanalytical data for the ligands and new complexes are given in Table 3). Analysis by DSC was carried out on a Perkin-Elmer DSC7 instrument using heating and cooling rates of 10 K min^{-1}. Analysis by hot stage microscopy was carried out using a Zeiss Labpol microscope equipped with a Link-Am TH600 hot stage and PR600 controller.

The XRD patterns were obtained as follows. The crude powder was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-Kα_1 beam (λ = 1.5418 Å) was obtained using a Guinier camera with a sealed-tube generator (900 W) with a bent quartz monochromator and an electric oven. The diffraction patterns were registered on an image plate. Periodicities were calculated from the position of the reflection at the smallest Bragg angle, which was in all cases the most intense. Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ±0.3 °C. In each case, exposure times were varied from 1 to 24 h.

Crystal data: $C_{14}H_{13}NO$, M_r = 211.25, orthorhombic, space group *Iba*2, *a* = 9.2463(18), *b* = 33.461(7), *c* = 7.2285(14) Å, *U* = 2236.4(8) Å^3, *Z* = 8, D_c = 1.255 g cm^{-3}, μ = 0.079 mm^{-1}, *F*(000) = 896, crystal size 0.6 × 0.3 × 0.08 mm. Data were collected at 150 K, on a Nonius-KappaCCD area detector diffractometer, at the window of a Nonius FR591 rotating anode X-ray generator (λ(Mo-Kα) = 0.71073 Å). Combined φ and ω scans, frame increment of 2.0°, θ_{max} = 27.49° (index ranges $-11 \leqslant h \leqslant 11$, $-41 \leqslant k \leqslant 43$, $-8 \leqslant l \leqslant 9$). An absorption correction was applied by comparison of multiple and symmetry equivalent reflections, using the program SORTAV.[20] A solution was obtained *via* direct methods and refined[21] by full-matrix least-squares on F^2, with hydrogen atoms included in idealised positions. 2481 unique data were produced from 7063 measured reflections (R_{int} = 0.0717). 147 parameters refined to R_1 = 0.0576 and wR_2 = 0.1372 [$I > 2\sigma(I)$] (R_1 = 0.0722 and wR_2 = 0.1471 for all data), with residual electron densities of 0.209 and −0.273 e Å^{-3}.

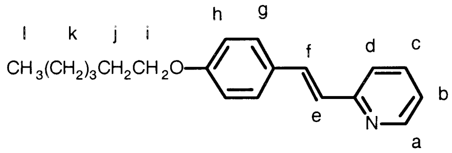
CCDC reference number 186196.

See http://www.rsc.org/suppdata/jm/b2/b204820e/ for crystallographic data in CIF or other electronic format.

Preparation of 4-alkyloxy-2′-stilbazole

The preparation of 4-hexyloxy-2′-stilbazole will be described and other homologues were prepared in the same way.

4-Hexyloxy(iodo)benzene (15.00 g, 49.3 mmol) and palladium acetate (0.111 g, 0.49 mmol) were placed in a thick-walled, Fisher–Porter vessel which was then degassed and placed under an atmosphere of nitrogen. 2-Vinylpyridine (6.220 g, 59.2 mmol) and triethylamine (5.700 g, 56.3 mmol) were added followed by acetonitrile (20 cm^3). The tube was then flushed again with nitrogen and placed at constant volume. The mixture was heated with stirring to 100 °C for 96 h. After this time the reaction was stopped and all of the solvent was removed *in vacuo* to give a brown solid, which was dissolved in dichloromethane (200 cm^3) and washed with water (2 × 100 cm^3). The organic phase was dried over sodium sulfate and the solvent was removed *in vacuo* leaving a yellow–brown solid. This was extracted repeatedly into petroleum ether (or hexane) using Soxhlet apparatus over 15 h. On cooling of the solvent, a fluffy white solid precipitated which was filtered and dried to give the product (11.5 g, 41.0 mmol, 83.2%)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (1H, dd, Ha, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 1.76 Hz), 7.60 (1H, ddd, Hc, 2 × $^3J_{HH}$ = 7.66 Hz, $^4J_{HH}$ = 1.76 Hz), 7.53 (1H, AB, Hf, $^3J_{HH}$ = 15.97 Hz),

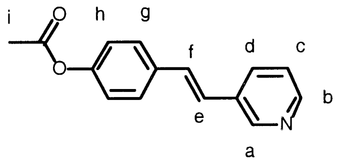
Table 3 Microanalytical data for the ligands and new complexes

				Calculated (found) (%)		
Compound	*n*	Yield (%)	Mp/°C	C	H	N
2	4	35	83.5	80.6 (80.2)	7.6 (7.7)	5.5 (5.4)
	5	39	74.7	80.9 (80.0)	7.9 (8.0)	5.2 (5.0)
	6	83	78.7	81.1 (81.2)	8.2 (8.6)	5.0 (4.8)
	7	53	92.9	81.3 (81.5)	8.5 (8.8)	4.7 (4.6)
	8	66	87.1	81.5 (81.9)	8.8 (9.2)	4.5 (4.4)
	12	39	85.3	82.1 (82.2)	9.7 (10.0)	3.8 (3.7)
3	4	40	87.0	80.6 (80.4)	7.6 (7.5)	5.5 (5.5)
	8	51	80.5	80.5 (81.1)	8.8 (8.8)	4.5 (4.5)
	12	56	84.1	82.1 (81.9)	9.7 (9.7)	3.8 (3.9)
4	4	42	114.7	62.8 (62.6)	7.2 (7.3)	3.2 (3.0)
	5	38	115.9	63.5 (63.3)	7.4 (7.6)	3.1 (2.8)
	6	46	87.4	64.2 (64.2)	7.7 (7.6)	3.0 (3.1)
	7	45	78.5	64.8 (64.8)	7.8 (8.0)	2.9 (2.6)
	8	30	86.9	65.4 (65.0)	8.0 (8.2)	2.8 (2.7)
	12	49	79.4	67.4 (67.3)	8.7 (8.9)	2.5 (2.4)
5	4	32	182.7	55.0 (54.9)	5.0 (4.9)	3.7 (3.5)
	8	46	154.2	59.0 (58.4)	6.2 (6.1)	3.2 (3.0)
	12	99	142.0	62.0 (61.6)	7.1 (7.2)	2.8 (2.6)
6	4	43	154.2	62.8 (62.3)	7.2 (7.2)	3.2 (3.2)
	8	53	146.2	65.4 (65.0)	8.0 (8.2)	2.8 (2.6)
	12	35	139.0	67.4 (67.4)	8.7 (8.9)	2.5 (2.3)

7.46 (1H, AA′XX′, Hg, J = 8.8 Hz), 7.30 (1H, d, Hd, $^3J_{HH}$ = 7.66 Hz), 7.09 (1H, dd, Hb, $^3J_{HH}$ = 7.66 Hz, $^3J_{HH}$ = 4.2 Hz), 6.99 (1H, AB, He, ^3J = 15.97 Hz), 6.85 (1H, AA′XX′, H_h, J = 8.8 Hz), 3.93 (2H, t, H_i, $^3J_{HH}$ = 6.45 Hz), 1.76 (2H, m, Hj), 1.41 (6H, m, Hk), 0.86 (3H, t, Hl, $^3J_{HH}$ = 6.69 Hz).

Preparation of 4-acetoxy-3′-stilbazole

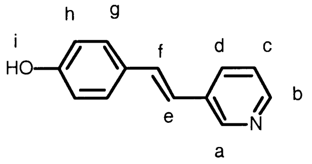
Herrmann's catalyst (0.206 g, 0.22 mmol) was placed in a thick-walled Pyrex Fisher–Porter vessel which was then degassed and placed under an atmosphere of nitrogen. 4-Acetoxystyrene (5.000 g, 30.8 mmol), 3-bromopyridine (3.480 g, 22.0 mmol) and triethylamine (2.780 g, 27.5 mmol) were added followed by acetonitrile (20 cm^3). The tube was then flushed again with nitrogen and then placed at constant volume. The mixture was heated with stirring to 100 °C for 96 h. After this time the reaction was stopped and all of the solvent was removed *in vacuo* to give an off-white solid. This was dissolved in dichloromethane (200 cm^3) and washed with water (2 × 100 cm^3). The organic phase was dried over sodium sulfate and the solvent was removed *in vaccuo*. The resulting solid was extracted repeatedly into hexane using Soxhlet apparatus over 15 hours. On cooling of the solvent, a fluffy white solid precipitated which was filtered and dried to give the product (3.2 g, 13.2 mmol, 60.0%).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (1H, d, Ha, $^4J_{HH}$ = 1.8 Hz), 8.58 (1H, dd, Hb, ^3J = 4.82 Hz, $^4J_{HH}$ = 1.8 Hz), 7.90 (1H, ddd, Hd, $^3J_{HH}$ = 7.89 Hz, 2 × $^4J_{HH}$ = 1.8 Hz), 7.61 (2H, AA′XX′, Hg, J = 8.48 Hz), 7.37 (1H, dd, Hc, $^3J_{HH}$ = 7.89 Hz, $^3J_{HH}$ = 4.82 Hz), 7.21 (3H, m, Hf, Hh), 7.10 (1H, d, He, ^3J = 16.32 Hz), 2.39 (3H, s, Hi).

Preparation of 4-hydroxy-3′-stilbazole

Potassium hydroxide (2.82 g, 50.4 mmol) was dissolved in a minimal amount of water (2.5 cm^3) and was added to 4-acetoxy-3'-stilbazole dissolved in ethanol (51 cm^3). The mixture was stirred at reflux for 3 hours and resulted in a yellow solution. After cooling, a solution of hydrochloric acid (10%) was added with stirring until pH = 6 and the formation of a white precipitate was observed. The mixture was then stirred at room temperature for 1 hour. It was then heated again to reflux and more ethanol was added (50 cm$^{3)}$). The precipitate dissolved and the solution was decanted from any remaining residual impurities. Upon cooling an off-white solid precipitated and was used without further purification.

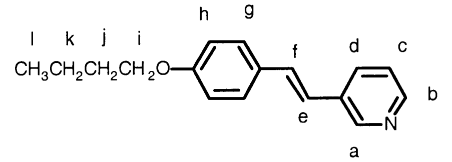


^{1}H NMR (300 MHz, DMSO): δ = 8.75 (1H, d, Ha, $^4J_{HH}$ = 2.0 Hz), 8.40 (1H, dd, Hb, $^3J_{HH}$ = 4.78 Hz, $^4J_{HH}$ = 1.5 Hz), 7.98 (1H, ddd, Hd, $^3J_{HH}$ = 7.98 Hz, 2 × $^4J_{HH}$ = 1.8 Hz), 7.42 (2H, AA′XX′, Hg, J = 8.67 Hz), 7.36 (1H, dd, Hc, $^3J_{HH}$ = 4.78 Hz, $^3J_{HH}$ = 7.98 Hz), 7.27 (1H, AB, Hf, J = 16.39 Hz), 7.01 (1H, AB, He, J = 16.39 Hz), 6.81 (2H, AA′XX′, Hh, J = 8.67 Hz);

Preparation of 4-alkyloxy-3′-stilbazole

The preparation of 4-butyloxy-3′-stilbazole will be described and other homologues were prepared in the same way.

1-Bromobutane (1.01 g, 7.4 mmol), 4-hydroxy-3′-stilbazole (1.5 g, 7.6 mmol) and caesium carbonate (4.95 g 15.2 mmol) were placed in a flask along with dibenzo-18-crown-6 (3 mg). DMF (30 cm^3) was added and the mixture was stirred at room temperature for 24 h. Water (100 cm^3) was then added and the product was extracted into toluene (2 × 100 cm^3). The toluene phase was washed with sodium hydroxide solution (5%, 100 cm^3) and water until pH = 7. The solvent was removed *in vacuo* and the resulting off-white solid was crystallised from hexane (0.757 g, 2.1 mmol, 40%).



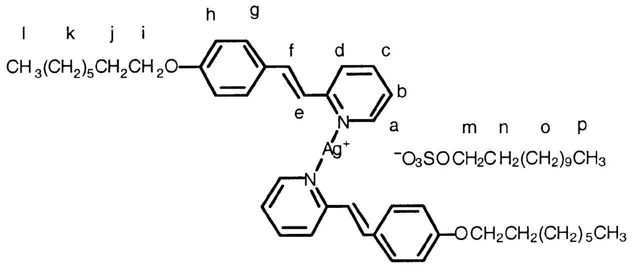
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (1H, d, Ha, $^4J_{HH}$ = 2.0 Hz), 8.48 (1H, dd, Hb, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz), 7.83 (1H, ddd, Hd, $^3J_{HH}$ = 8.04 Hz, 2 × $^4J_{HH}$ = 1.7 Hz), 7.47 (2H, AA′XX′, Hg, J = 8.69 Hz), 7.29 (1H, dd, Hc, $^3J_{HH}$ = 4.7 Hz, $^3J_{HH}$ = 8.04 Hz), 7.14 (1H, AB, Hf, J = 16.40 Hz), 6.93 (1H, AB, He, J = 16.40 Hz), 6.91 (2H, AA′XX′, Hh, J = 8.69 Hz), 4.01 (2H, t, Hi, $^3J_{HH}$ = 6.59 Hz), 1.80 (2H, m, Hj), 1.56 (2H, m, Hk), 1.01 (1H, t, Hl, $^3J_{HH}$ = 7.39 Hz).

Preparation of bis(4-alkyloxy-2′-stilbazole)silver(I) dodecyl sulfate (4)

All homologues were made by the same method as for bis(4-octyloxy-2′-stilbazole)silver(I) dodecyl sulfate which is described. Bis(4-alkyloxy-3′-stilbazole)silver(I) dodecyl sulfates (**6**) were made in the same way.

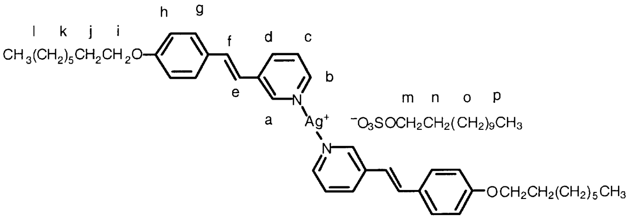
In a flask, protected from light, equipped with a dropping funnel, was placed silver(I) dodecyl sulfate (0.150 g, 0.40 mmol). The flask was degassed and placed under nitrogen. Dichloromethane (10 cm^3) was added and the suspension was stirred. 4-Octyloxy-2′-stilbazole (0.228 g, 0.84 mmol) dissolved in dichloromethane (10 cm^3) was added dropwise and the mixture was stirred at room temperature for 15 h. The resulting yellow solution was filtered through Celite to remove any unreacted silver(I) dodecyl sulfate. The solvent was evaporated and the yellow solid was crystallised from hot acetone leaving a slightly yellow crystalline solid (0.105 g, 0.12 mmol, 30.0%). Some homologues were crystallised from methanol.

Bis(4-octyloxy-2′-stilbazole)silver(I) dodecyl sulfate.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (2H, dd, Ha, $^3J_{HH}$ = 4.52, Hz, $^4J_{HH}$ = 1.47 Hz), 7.80 (2H, ddd, Hc, 2 × $^3J_{HH}$ = 7.70 Hz, $^4J_{HH}$ = 1.47 Hz), 7.66 (2H, d, Hd, $^3J_{HH}$ = 7.92 Hz), 7.30 (8H, m, Hb, Hf, Hg), 7.16 (2H, AB, He, ^3J = 16.15 Hz), 6.75 (4H, AA′XX′, Hh, J = 8.72 Hz), 4.11 (2H, t, Hm, $^3J_{HH}$ = 6.87 Hz), 3.93 (4H, t, Hi, $^3J_{HH}$ = 6.57 Hz), 1.77 (4H, m, Hj), 1.59 (2H, m, Hn), 1.35 (38H, m, Hk, Ho), 0.89 (9H, m, Hl, Hp).

Bis(4-octyloxy-3′-stilbazole)silver(I) dodecyl sulfates.

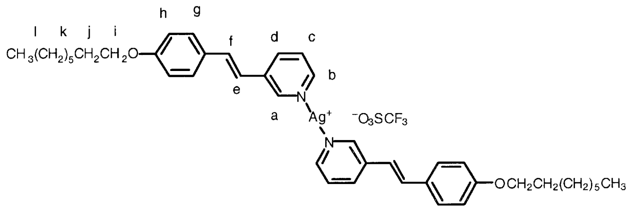


^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.94$ (2H, d, Ha, $^4J_{HH} = 1.73$ Hz), 8.61 (2H, d, Hb, $^3J_{HH} = 5.26$ Hz, $^4J_{HH} = 1.73$ Hz), 7.81 (2H, ddd, Hd, $^3J_{HH} = 7.99$ Hz, $2 \times {}^4J_{HH} = 1.73$ Hz), 7.44 (4H, AA′XX′, Hg, $J = 8.81$ Hz), 7.33 (2H, dd, Hc, $^3J_{HH} = 5.26$ Hz, $^3J_{HH} = 7.99$ Hz), 7.22 (2H, AB, Hf, $^3J_{HH} = 16.37$ Hz), 6.87 (4H, AA′XX′, Hh, $J = 8.81$ Hz), 6.84 (2H, AB, He, $^3J_{HH} = 16.37$ Hz), 4.15 (2H, t, Hm, $^3J_{HH} = 6.87$ Hz), 3.97 (4H, t, Hi, $^3J_{HH} = 6.57$ Hz), 1.80 (4H, m, Hj), 1.67 (2H, m, Hn), 1.35 (38H, m, Hk, Ho), 0.89 (9H, m, Hl, Hp).

Preparation of bis(4-alkyloxy-3’-stilbazole)silver(I) triflate (5)

All homologues were made by the same method as for bis(4-octyloxy-3′-stilbazole) silver(I) triflate which is described.

4-Octyloxy-3′-stilbazole (0.06 g, 0.19 mmol) and silver(I) triflate (0.025 g, 0.097 mmol) were placed in a flask protected from light which was then flushed with nitrogen. Acetone (5 cm^3) was added and the mixture was stirred at room temperature for 4 h. After cooling in ice the colourless precipitate was filtered off and was washed with cold acetone giving a colourless solid of analytical purity (0.039 g, 0.045 mmol, 46%).



^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.83$ (2H, d, Ha, $^4J_{HH} = 1.6$ Hz), 8.53 (2H, dd, Hb, $^3J_{HH} = 5.2$ Hz, $^4J_{HH} = 1.6$ Hz), 7.70 (2H, ddd, Hd, $^3J_{HH} = 8.04$ Hz, $2 \times {}^4J_{HH} = 1.6$ Hz), 7.39 (4H, AA′XX′, Hg, $J = 8.6$ Hz), 7.24 (2H, dd, Hc, $^3J_{HH} = 5.2$ Hz, $^3J_{HH} = 8.05$ Hz), 7.14 (2H, AB, Hf, $J = 16.4$ Hz), 6.83 (4H, AA′XX′, Hh, $J = 8.6$ Hz), 7.72 (2H, AB, He, $J = 16.4$ Hz), 3.97 (4H, t, Hi, $^3J_{HH} = 6.7$ Hz), 1.84–1.77 (4H, m, Hj), 1.39–1.33 (20H, m, Hk), 0.92–0.86 (6H, t, Hl, $^3J_{HH} = 6.9$ Hz).

Acknowledgements

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