Liquid-crystalline, polycatenar complexes of silver(I): dependence of the mesomorphism on the ligand and the anion

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We have synthesised several series of poly(alkoxy)stilbazole ligands, and investigated the thermal behaviour of their complexes with some silver salts. Most of the complexes, with the general formula $[\mathrm{AgL_2}][\mathrm{X}]$, where X = dodecyl sulfate (DOS) or trifluoromethanesulfonate (OTf), and L = poly(alkoxy)stilbazole, were found to be liquid-crystalline over a wide-temperature range, the vast majority of them being low-melting. The mesomorphic properties were mainly dominated by the formation of hexagonal columnar ($\mathrm{Col_h}$) phases and to a lesser extent, of bicontinuous $Ia\bar{3}d$ cubic phases; monotropic nematic and smectic C phases were also seen for one structural type of compound only. The mesophases were assigned on the basis of their optical textures under polarised optical microscope (POM) prior to being identified by X-ray diffraction (XRD). The temperatures and enthalpies of the transitions were determined by differential scanning calorimetry (DSC). The mesomorphism was found to be strongly dependent on the substitution pattern of the ligand, that is on the number, position and length of alkoxy chains, as well as on the type of the counter anion. We explain the mesomorphism in terms of ionic interactions and in terms of mean interfacial curvature between the hydrophobic, aliphatic chains and the rigid, aromatic, central core, by analogy to lyotropic systems.

Introduction

For many years, thermotropic cubic phases were scarcely studied, essentially due to their rare appearance in conventional liquid-crystalline materials,[1] and thus, very little information was known about their structure. More recently, they have been more extensively studied. The two general types of cubic phases[2,3] commonly found in lyotropic systems are now being observed in many thermotropic systems. For instance, micellar thermotropic cubic phases (analogous to the lyotropic $\mathrm{I_1}$ and $\mathrm{I_2}$ phases) have been undoubtedly identified in some dendrimeric macromolecules,[4] in several mesogens containing a carbohydrate or a polyhydroxy moiety,[5] and also, most probably, in some polar, globular mesogens.[6] Bicontinuous thermotropic cubic phases (analogous to the lyotropic $\mathrm{V_2}$ phase) have been observed in some more conventional systems, for instance in calamitic systems such as the 4-alkoxy-3-nitro- (or -cyano) biphenyl-4′-carboxylic acids and 1,2-bis(4-alkoxybenzoyl)hydrazine,[7] disc-like compounds such as the hexa-*O*-pentanoylscyllo inositol and a few derivatives of the ellagic acids,[8] as well as in polyol and carbohydrate liquid crystals,[5a,9] silver stilbazole complexes,[10] polycatenar and bi-swallow-tailed mesogens,[11] dialkylphosphate salts,[12] oligoalkylene amides,[13] rod-coil calamitic mesogens[14] and, probably, in some silver thiolate complexes.[15] Other mesomorphic systems have been found to form cubic phases in the melt, such as diblock co-polymers[16] in which the mesophases occur as a function of the volume fraction of the two blocks, and polyelectrolyte–surfactant systems.[17] With such a variety of molecular structures, it is not straightforward to predict the occurrence of these three-dimensional mesophases and thus, the possibility for molecular design remains low. However, one can notice that most of the compounds listed above possess a common denominator, in that they are amphiphilic in nature. Indeed, all the molecules listed above are made of two (or more) different constituent blocks which are structurally and chemically different.

The concept of amphiphilicity and liquid-crystallinity was, for a long time, used exclusively to describe the behaviour of lyotropic liquid crystal systems. More recently, the amphiphilic character of thermotropic mesogens has been taken into account and is felt to be a very important driving force for thermotropic mesophase formation.[18] Consequently, it is now common to remark on the similarities in the mesomorphism of thermotropic and lyotropic mesogens, rather than look to the differences. This approach, developed in two major papers[18] which emphasise the amphipatic character of the molecules, should progressively set up the foundation of a new concept unifying the description of mesophases on the one hand, and leading to enhanced understanding of phase formations and transitions based on the evolution of the shape of the interfaces on the other. This concept has been the subject of an updated comprehensive review recently published, which highlights the importance of micro-segregation in non-conventional mesogens, and further extends the essential role of amphipathy in liquid crystals.[19]

Indeed, an important property of amphiphilic molecules, due to the different nature of their block units, is the ability to organise to form structures which divide the space into sub-spaces with different properties, the different sub-spaces thus being separated by interfaces. The degree of amphiphilic character, in addition to the degree of molecular anisometry, will influence the micro-segregation and affect the shape of the surface (interface) separating the different parts of the molecules. Bearing this in mind, a lamellar phase can, therefore, be described as a succession of planar surfaces, and a columnar phase as a two-dimensional arrangement of cylindrical surfaces. However, since this is purely a geometrical approach, care must be taken as these interfaces are not so precise and well-defined, and in addition to thermal agitation, diffusion

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occurs so that the interfaces can be modulated (smectic) or undulating (columnar), *i.e.* the interfaces are not planar, rather curved with a wave-like periodicity (see *e.g.* refs 11*a* and 12*c*). Furthermore, transitions from smectic or columnar organisation to nematic phases can be explained by molecular diffusion from adjacent lamellar planes (S-to-N), or adjacent columns (Col-to-N) until the interfaces have totally vanished.

In the last 15 years, there has been a growing attraction to the study of metallomesogens, as evidenced by an abundant literature.[20] This interest arose because of the new properties that may be expected on the introduction of metals into liquid-crystalline materials. In addition, metals offer wider possibilities for structural variations (coordination, geometry) than simple organic molecules, and a large number of metal–ligand combinations can be envisaged to generate mesomorphic materials.[20] Another interesting aspect is the search for the establishment of well defined structure–property relationships in order to be able to predict liquid-crystalline properties in metallomesogens, as well as to enrich our understanding of phase formation and molecular organisation, since additional parameters than those considered in organic liquid crystals may have to be taken into account. Many such studies have already been undertaken,[20] and, in particular, an important part of our work has concentrated on the silver(I) complexes of alkoxystilbazoles.[11,20b,21] In a previous study, we described the mesomorphism of some bis(3,4-dialkoxystilbazole)silver(I) alkyl sulfate complexes, and were particularly interested in determining the factors governing the formation of the cubic mesophases present in these systems.[11a,21] A part of this work consisted of varying the length of the alkyl sulfate anion only, and we remarked that the mesophase range and type were dependent on whether or not the (alkyl sulfate) alkyl chain crossed the aliphatic/aromatic interface.[21] This was explained in terms of contribution (or not) of the anion alkyl chain to the molecular chain area, resulting in the modification (increase) of the aliphatic/aromatic ratio, and hence, of the degree of curvature at the core–chain interface. Thus, a possible way to obtain mesomorphic materials with "curved mesophases" (cubic and columnar phases) is to vary the aliphatic/aromatic ratio of amphiphilic molecules in order to modify the associated interface, by analogy with the lyotropic mesophases. As was previously shown,[11a] this can be achieved, for example, by grafting more than one peripheral chain on the mesogen, which can be approximated, in some ways, to the addition of an apolar solvent to amphiphilic molecules. We now report a further development of this work in which we focus primarily on the structure of the ligand, and thus, we have synthesised five more series of polysubstituted stilbazoles in order to observe and try to rationalise some effects on the thermal behaviour of the resulting silver complexes. Furthermore, two different silver salts were used: silver(I) dodecyl sulfate (AgDOS) and silver(I) trifluoromethanesulfonate (AgOTf).

Results

Synthesis and characterisation of the ligands and their complexes

The synthetic pathway used to prepare the ligands and the silver complexes is shown in the scheme below. 2,4-Di-, 2,3,4-tri- and 2,4,5-tri-alkoxybenzaldehydes were obtained directly by etherification of the corresponding di- or tri-hydroxybenzaldehydes (Scheme 1, route 2) with the appropriate 1-bromoalkane, under Williamsom ether conditions, in butanone or pentan-2-one (the latter being found considerably to ameliorate the yield of the *O*-alkylation reaction). However, 3,5-di- and 3,4,5-tri-alkoxybenzaldehydes were prepared differently in three steps due to the high cost of the parent hydroxybenzaldehyde (Scheme 1, route 1). The first step consisted of the etherification of methyl 3,5-di- and 3,4,5-tri-hydroxybenzoates with 1-bromoalkane. The resulting methyl poly(alkoxy)benzoates were then reduced to the corresponding benzyl alcohol using lithium tetrahydroborate ($LiBH_4$) in a 5 : 1 EtOH–THF mixture, and the alcohols were finally oxidised by pyridinium chlorochromate (PCC) in dichloromethane to furnish the desired poly(alkoxy)benzaldehydes.[22] The poly(alkoxy)stilbazoles were synthesised, as described previously, by condensation of the poly(alkoxy)benzaldehydes with 4-methylpyridine using lithium diisopropylamide (LDA[23]) in THF, and followed by the dehydration of the intermediate alcohols by pyridinium toluene-*p*-sulfonate salt (PPTS) in toluene at reflux, the water formed being continuously removed from the reaction mixture by the use of a Dean–Stark apparatus. The complexes were subsequently prepared by stirring two equivalents of stilbazole with one equivalent of the silver salt in dichloromethane (for AgDOS), or in acetone (for AgOTf), at ambient temperature and with the vessel protected from light.

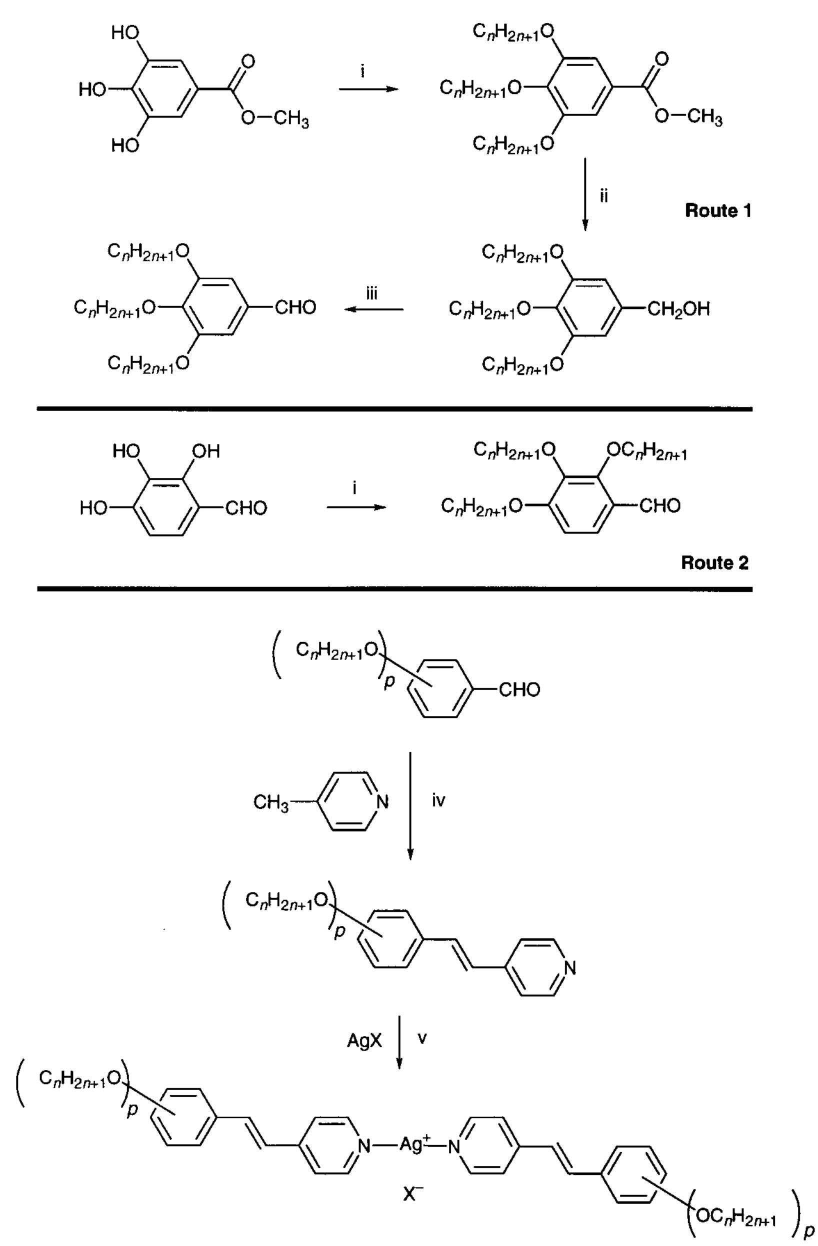
The NMR spectroscopic data, ^{1}H, ^{13}C and ^{19}F, were in agreement with the proposed structures of the intermediates and final substances, and the purity was confirmed by elemental analysis (C,H,N,S). All the stilbazoles were *trans* as evidenced by ^{1}H NMR, in which the coupling constant of the AB system was *ca.* 16–16.5 Hz. The complexes generate almost identical spectra to the free ligands (for which the *trans* configuration of the double bond was retained), although some appreciable differences in chemical shifts (^{1}H and ^{13}C) indicated that the complexation was achieved. ^{13}C and ^{19}F NMR clearly showed that the triflate complexes were formed, as in the carbon spectra, a quartet was observed at δ 121 corresponding to the C–F coupling, with a $^1J_{CF} = 320$ Hz, as well as a singlet (CF_3) in the fluorine spectra at δ *ca.* -80.

Thermal behaviour of the stilbazoles

The ligands will be abbreviated hereafter as St(*n*-*x*,*y*,*z*), where *n* represents the number of carbon atoms in the flexible, alkoxy chains, and *x*, *y* and *z* the position of the alkoxy chains grafted on the terminal benzene ring [*e.g.* St(6-3,4) represents 3,4-dihexyloxystilbazole]. None of the stilbazoles was mesomorphic.[24] The loss of the liquid-crystalline properties was nevertheless expected owing to the considerable reduction in the molecular anisotropy resulting from the grafting of more than one alkoxy chains in the 2- and/or 3-positions of the terminal benzene ring. However, they were noticeable for their low-melting temperatures (Table 6), some of them did even not crystallise but remained as oils instead, a desired condition since when complexed to silver, the metal complexes should equally show a substantial decrease in the transition temperatures.

Thermal behaviour of the complexes

In general, the melting points of the complexes described here were significantly lower than that of the 'parent' complexes, bis(4′-alkoxy-4-stilbazole)silver(I) dodecyl sulfate[11b] and triflate,[25] showing that the grafting of several alkoxy chains in the periphery of the complex can be a productive approach to obtain low-melting materials. A consequence of this important depression in the melting temperatures of the mesomorphic complexes is reflected by the observation of larger mesomorphic domains than in the corresponding parent systems, since the clearing points remained almost unchanged. At first glance, it seems that the type of mesophase was more dependent on the substitution pattern of the ligand than the type of anion (*vide infra*). However, appreciable differences between the DOS series and the OTf series of polycatenar mesogens were found for the melting points of the complexes, which were higher in the triflate series. This we largely attribute to a greater degree of ionic character in the silver–anion inter-



Scheme 1 Synthesis of the stilbazoles and their complexes. i, $C_nH_{2n+1}Br$, K_2CO_3, butanone or pentan-2-one, reflux, 24 h; ii, $LiBH_4$, THF–MeOH (5 : 1), N_2, reflux, 12 h; iii, PCC, CH_2Cl_2, r.t., 4 h; iv, LDA, THF, −78 °C, N_2, 12 h; H_2O–HCl, r.t., 2 h; PPTS, toluene, reflux, 12 h; v, AgX, CH_2Cl_2 or acetone, r.t., 4 h.

action, thus requiring more energy to break down the lattice. This is supported by the stronger tendency of the triflate complexes to crystallise on cooling, when compared to their dodecyl sulfate analogues.[11b,c,25] For all the mesomorphic complexes described here, the mesophases were characterised initially by optical microscopy, the nematic (N), smectic C (S_C), cubic (Cub) and columnar (Col) phases giving characteristic textures[1] and the transition temperatures detected by DSC analysis.

Thermal behaviour of the silver(I) dodecyl sulfate complexes

The mesomorphism of the [AgSt(*n*-3,4)$_2$][DOS] has already be described,[11a] but will be recalled here in order to act as a reference (Fig. 1). Thus, a bicontinuous $Ia\bar{3}d$ cubic phase (Cub) was seen for $4 \leqslant n \leqslant 10$ and a hexagonal columnar phase (Col_h) for $6 \leqslant n \leqslant 12$. The domains of mesophase stability were fairly large, especially those of the columnar phases, with melting points in the range 55 to 70 °C, and clearing points varying between 100 and 170 °C (Table 1).

Complexation of St(*n*-3,5) to silver(I) dodecyl sulfate also induced strongly mesomorphic materials, which are unique examples of mesomorphic tetracatenar mesogens having four chains in the *meta* positions and only four aromatic rings.[12] Thus, complexes with $n = 6$–14 were mesomorphic showing one type of mesophase from almost room temperature up to 90–120 °C (Fig. 2). The low-melting behaviour is likely connected to the *meta* position of all the chains, and the absence of chains in the *para* positions. On the basis of the optical texture, the phase was assigned as columnar, and the presence of large homeotropic areas further suggested the symmetry of the mesophase to be hexagonal (uniaxial). Some of the complexes were obtained as amorphous solids, and on cooling from the isotropic liquid, they did not crystallise, although the mesophase was not fluid below the temperature where the compounds were expected to crystallise. In the following heat–cool cycles, no sign of crystal-to-columnar phase transition could be detected by DSC, and the optical texture of the mesophase was preserved as seen in the optical microscope. This peculiar thermal behaviour is consistent with the formation of anisotropic liquid-crystalline glasses (in the present case columnar glasses),[26] although we were not able to obtain T_g and ΔC_p from what turned out to be a poorly resolved DSC trace. The tetradecyloxy homologue presents two meso-

Table 1 Transition temperatures and thermal data for $[\mathrm{AgSt}(n\text{-}3,5)_2][\mathrm{DOS}]$ and $[\mathrm{AgSt}(n\text{-}2,4)_2][\mathrm{DOS}]$

Complex	n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J mol^{-1} K^{-1}
$[\mathrm{AgSt}(n\text{-}3,5)_2][\mathrm{DOS}]$	1	Crys–I	160	—	—
	4	Crys–Crys′	98	8.4	22.6
		Crys–I	119	39.2	99.0
	6	Crys–$\mathrm{Col_h}$	32	4.8	15.6
		$\mathrm{Col_h}$–I	95	1.5	4.0
	7	g^a–$\mathrm{Col_h}$	34	—	—
		$\mathrm{Col_h}$–I	93	0.3	0.8
	9	g^a–$\mathrm{Col_h}$	29	—	—
		$\mathrm{Col_h}$–I	113	1.9	5.0
	12	Crys–$\mathrm{Col_h}$	32	14.3	46.9
		$\mathrm{Col_h}$–I	107	1.8	4.8
	14	Crys–$\mathrm{Col_{h1}}$	41	94.9	302.6
		$\mathrm{Col_{h1}}$–$\mathrm{Col_{h2}}$	76	14.8	42.5
		$\mathrm{Col_{h2}}$–I	123	1.9	4.8
$[\mathrm{AgSt}(n\text{-}2,4)_2][\mathrm{DOS}]$	7	Crys–Crys′	61	28.1	83.9
		Crys′–I	71	18.9	54.9
		(I–N)	(65)	—	
	14	Crys–I	57	90.3	273.4
		(I–N)	(53)	(−0.8)	(−2.6)
		(N–$\mathrm{S_C}$)	(50)	(−2.5)	(−7.6)

[a] g stands for frozen mesophase or anisotropic glass.

phases (a reversible transition was clearly observed by DSC), although no textural change was observed at the transition. XRD studies corroborated the optical observations in the sense that no structural change was detected. This may suggest a transition between two hexagonal columnar phases (the first order DSC transition is consistent with a transition between two phases of the same symmetry), with a different type of order (or disorder) in the molecular organisation within the columns, these columns being nevertheless associated according to a 2-D hexagonal array.

In the second set of complexes, namely $[\mathrm{AgSt}(n\text{-}2,4)_2][\mathrm{DOS}]$, only monotropic mesophases were observed (Table 1); for $n = 7$ this was a nematic phase, while for $n = 14$, both a nematic and a smectic C phase were observed. Both phases were recognised by their characteristic optical texture, and the N-to-$\mathrm{S_C}$ transition was readily detected both by DSC and optical microscopy (*e.g.* the formation of transition bars in the texture just before the transition). In both cases, crystallisation occured on reaching room temperature.

Amongst the hexa-substituted substances, only the $[\mathrm{AgSt}(n\text{-}3,4,5)_2][\mathrm{DOS}]$ complexes showed mesomorphic properties (Table 2). All the complexes from $n = 4$ to 14 showed the expected columnar mesophase (Fig. 3), over an extended temperature range ($\Delta T = 100$–$120\,°\mathrm{C}$). Most of them did not crystallise on cooling, retaining the texture of the mesophase, suggesting once more, the formation of anisotropic hexagonal columnar glasses, although the glass transition could not be observed by DSC.

The complexes of the other two series of compounds, $[\mathrm{AgSt}(n\text{-}2,3,4)_2][\mathrm{DOS}]$ and $[\mathrm{AgSt}(n\text{-}2,4,5)_2][\mathrm{DOS}]$, melted directly to the isotropic liquid without showing any mesophase on heating, nor any metastable phase on cooling. These complexes showed strong supercooling effects, but they eventually crystallised after a few hours.

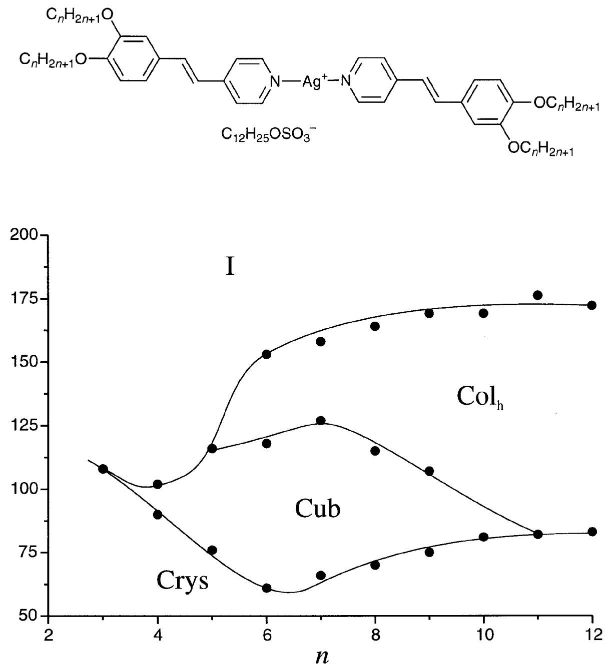


Fig. 1 Phase diagram for the complexes $[\mathrm{AgSt}(n\text{-}3,4)_2][\mathrm{DOS}]$.

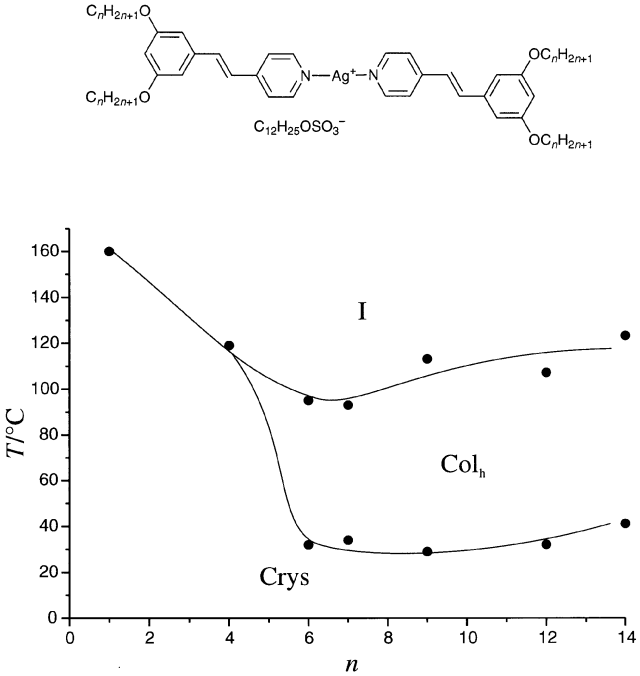


Fig. 2 Phase diagram for the complexes $[\mathrm{AgSt}(n\text{-}3,5)_2][\mathrm{DOS}]$.

Table 2 Transition temperatures and thermal data for [AgSt(n-3,4,5)$_2$]-[DOS]

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_{m}/J mol^{-1} K^{-1}
1	Crys–I	180	—	—
4	Crys–Crys′	42	2.3	7.3
	Crys′–Col$_{\mathrm{h}}$	53	9.9	30.3
	Col$_{\mathrm{h}}$–I	127	1.2	2.9
5	Crys–Col$_{\mathrm{h}}$	38	8.5	27.3
	Col$_{\mathrm{h}}$–I	133	2.1	5.1
6	Crys–Col$_{\mathrm{h}}$	34	7.0	22.8
	Col$_{\mathrm{h}}$–I	125	2.3	5.8
7	g^a–Col$_{\mathrm{h}}$	34	—	—
	Col$_{\mathrm{h}}$–I	141	3.0	7.2
8	g^a–Col$_{\mathrm{h}}$	30	—	—
	Col$_{\mathrm{h}}$–I	141	3.4	8.1
9	g^a–Col$_{\mathrm{h}}$	28	—	—
	Col$_{\mathrm{h}}$–I	141	3.2	7.9
10	g^a–Col$_{\mathrm{h}}$	32	—	—
	Col$_{\mathrm{h}}$–I	137	3.4	8.3
11	g^a–Col$_{\mathrm{h}}$	37	—	—
	Col$_{\mathrm{h}}$–I	133	3.9	9.5
14	Crys–Col$_{\mathrm{h}}$	41	87.6	278.9
	Col$_{\mathrm{h}}$–I	122	4.5	11.4

[a] g stands for frozen mesophase or anisotropic glass.

Table 3 Transition temperatures and thermal data for [AgSt(n-3,4)$_2$]-[OTf]

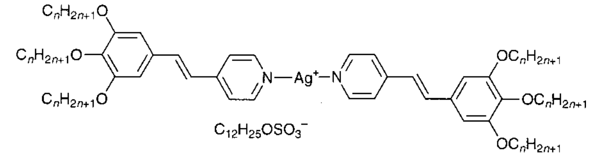
n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_{m}/J mol^{-1} K^{-1}
4	Crys–Crys′	138	12.8	31.3
	Crys′–I	188	37.6	81.7
6	Crys–Crys′	144	16.2	38.8
	Crys′–I	148	—	—
7	Crys–Crys′	132	18.7	46.2
	Crys′–Cub	138	3.9	9.5
	Cub–I	153	3.3	7.8
8	Crys–Crys′	72	1.9	5.6
	Crys′–Crys″	76	2.6	7.4
	Crys″–Crys‴	91	10.0	27.4
	Crys″–Cub	125	4.3	10.7
	Cub–I	154	3.1	7.2
10	Crys–Crys′	63	10.7	31.8
	Crys′–Crys″	88	55.2	152.6
	Crys″–Cub	99	4.8	13.0
	Cub–I	161	3.6	8.2
12	Crys–Cub	97	84.0	227.1
	Cub–I	164	3.7	8.6
13	Crys–Cub	96	89.7	242.9
	Cub–Col$_{\mathrm{h}}$	152	1.6	3.8
	Col$_{\mathrm{h}}$–I	166	—	—
14	Crys–Crys′	84	1.5	4.2
	Crys′–Cub	100	101.1	271.0
	Cub–Col$_{\mathrm{h}}$	149	2.3	5.6
	Col$_{\mathrm{h}}$–I	172	1.3	2.8
18	Crys–Crys′	81	21.1	59.6
	Crys′–Col$_{\mathrm{h}}$	101	125.6	335.6
	Col$_{\mathrm{h}}$–I	151	1.3	3.0

Thermal behaviour of the silver(I) triflate complexes

The first series of triflate complexes, [AgSt(n-3,4)$_2$][OTf], displayed a very rich mesomorphism (Table 3), in a way very similar to the corresponding dodecyl sulfate complexes,[11a] including both cubic and columnar mesophases (Fig. 4). The cubic phase was seen for almost all homologues ($7 \leqslant n \leqslant 14$), while the columnar phase appeared only for $n \geqslant 13$. XRD studies confirmed these observations; the space group of the cubic phase was assigned as $Ia\bar{3}d$, and the columnar phase has a 2-D hexagonal lattice. The temperature range of the cubic phase was found to increase until $n = 12$ (mainly on account of a rather pronounced reduction in melting point with increasing chain length) before it started to decrease, completely vanishing at the expense of the columnar phase at $n = 14$. For the compounds showing only the cubic phase, the transition to the isotropic liquid was easily seen as the distorted, imprisoned air-bubbles relaxed to a spherical shape, as already seen in some lyotropic systems.[27] The columnar phase also exists over a wide temperature range, as it does in the corresponding dodecyl sulfate series.

In the second series of complexes, [AgSt(n-3,5)$_2$][OTf] (Table 4), only the tetradecyloxy derivative was found to be mesomorphic, the optical texture suggesting a hexagonal columnar phase. The phase exists over a wide temperature range ($\Delta T = 70$ °C), with a melting point slightly above ambient (42 °C). On cooling, no crystallisation peak was seen by DSC, but it did appear in the following heat (cold crystallisation), followed by melting of the complex at 42 °C.

In the next series, [AgSt(n-2,4)$_2$][OTf] (Table 4), the two complexes synthesised ($n = 7$ and 14) exhibited a monotropic (metastable) nematic phase, in common with the analogous dodecyl sulfate salts, though the smectic C found in the latter



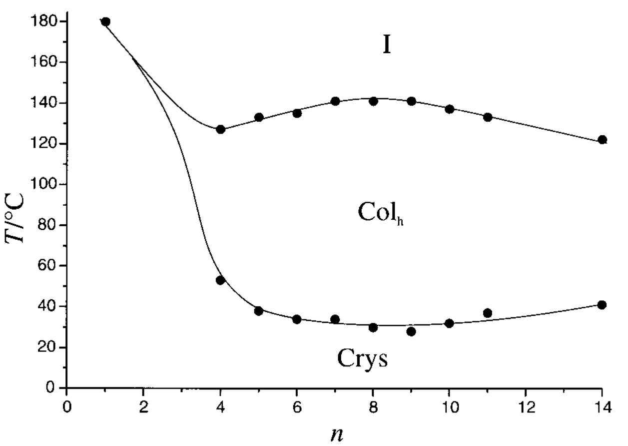
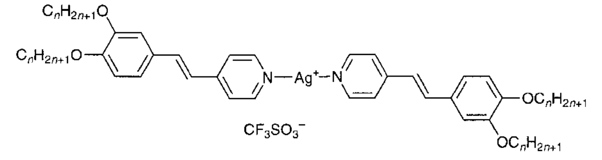


Fig. 3 Phase diagram for the complexes [AgSt(n-3,4,5)$_2$][DOS].



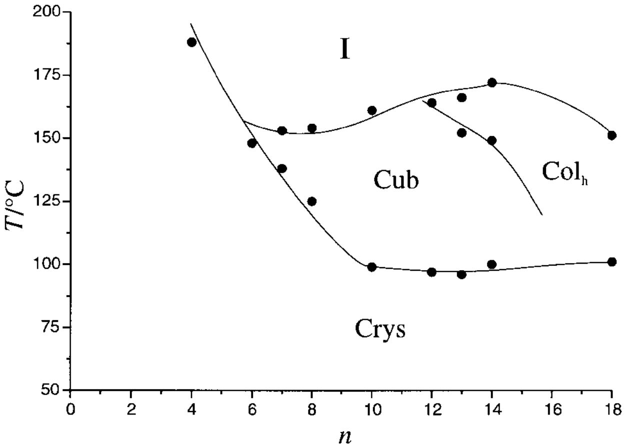


Fig. 4 Phase diagram for the complexes [AgSt(n-3,4)$_2$][OTf].

Table 4 Transition temperatures and thermal data for [AgSt(n-3,5)$_2$][OTf] and [AgSt(n-2,4)$_2$][OTf]

Complex	n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J mol^{-1} K^{-1}
[AgSt(n-3,5)$_2$][OTf]	6	Crys–I	124	18.7	47.1
	9	Crys–Crys′	45	8.0	25.1
		Crys′–I	81	6.5	18.3
	12	Crys–Crys′	35	8.2	26.4
		Crys′–I	59	3.4	10.4
	14	Crys–Col$_h$	42	92.9	294.8
		Col$_h$–I	112	2.7	6.9
[AgSt(n-2,4)$_2$][OTf]	7	Crys–Crys′	92	41.2	112.8
		Crys′–I	113	44.8	115.9
		(I–N)	(88)	(−1.2)	(−3.3)
	14	Crys–Crys′	50	10.8	33.4
		Crys′–I	81	94.5	267.1
		(I–N)	(78)	(−0.9)	(−2.7)

was absent here. The two compounds recrystallised a few degrees below the isotropic–nematic phase transition and showed this behaviour reproducibly in the following heat–cool cycles.

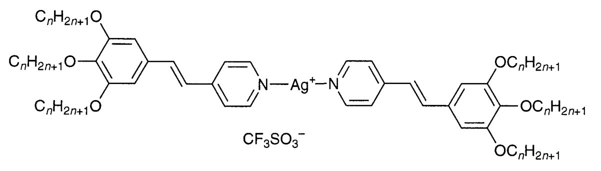
Of the hexacatenar complexes, [AgSt(n-2,3,4)$_2$][OTf] and [AgSt(n-2,4,5)$_2$][OTf] melted to the isotropic liquid at 100–120 °C for the octyloxy derivatives, and at 70–80 °C for the tetradecyloxy derivatives, with no metastable phase being detected on cooling from the isotropic liquid.

However, the complexes [AgSt(n-3,4,5)$_2$][OTf] (Table 5) exhibited a rather complicated thermal behaviour, and optical microscopy suggested the following sequence (Fig. 5). The butyloxy derivative melted at high temperature to the isotropic liquid without showing any mesophase. The hexyloxy and heptyloxy derivatives displayed a cubic phase, over a narrow temperature range, the phase being assigned by the growth of black, distorted domains until the whole area became completely optically extinct. The phase this produced was also rather viscous. The transitions were confirmed by DSC, showing a broad peak at the crystal-to-cubic phase transition, and another first order peak for the clearing point. The octyloxy homologue showed a rather unusual mesomorphism. Indeed, the optical observations, in addition to the DSC traces, suggested that the silver complex crystallised as two different, thermodynamically stable polymorphic crystals. On heating, a first transition at 53 °C gave rise to a biphasic region, comprising a cubic phase and a crystalline phase, Crys′. The preparation was maintained at 60–62 °C for two hours to see whether this phenomenom was due to the slow kinetics of the crystal-to-cubic phase transition, thus, explaining the delay in the melt of the crystal phase, or whether Crys′ was another thermodynamically stable crystalline structure. No change was observed, suggesting that the initial bulk compound contained two different crystalline phases. On further increasing the temperature, the crystalline phase, Crys′, melted to give a columnar mesophase, Col$_h$, at 65 °C, the phase being recognisable by its optical texture. In this temperature range, two mesophases were thus co-existing, a cubic and a columnar phase. Here again, the preparation was left for two hours at 95 °C, but no change was observed. At 100 °C, the cubic phase melted to a columnar phase, Col$'_h$. Surprisingly, the two columnar phases were not miscible as evidenced by large boundaries between the two textures, although they displayed identical defects. The mesophases did not mix when pressure was applied on the cover-slip, nor when the temperature was kept at 105 °C for two hours. Anyway, the non-miscibility of the two columnar mesophases does not necessarily contradict their possible identical nature. At 108 °C, the columnar phase Col$_h$ melted to the isotropic liquid, and the other Col$_{h'}$ eventually melted at 127 °C. On cooling, the same mesophases and biphasic regions were again observed, and this behaviour was reproducible on subsequent heat–cool cycles. The presence of a cubic phase in this series was rather unexpected, and there is

Table 5 Transition temperatures and thermal data for [AgSt(n-3,4,5)$_2$][OTf]

n	Transition	T /°C	ΔH /kJ mol^{-1}	ΔS_m /J mol^{-1} K^{-1}
4	Crys–I	205	—	—
6	Crys–Cub	99	10.8	29.0
	Cub–I	113	0.9	2.4
7	Crys–Cub	107	7.1	18.8
	Cub–I	121	3.8	9.6
8[a]	Crys–Cub + Crys′	53	7.6	23.3
	Cub + Crys′–Cub + Col$_h$	65	3.1	9.1
	Cub + Col$_h$–Col$_{h'}$ + Col$_h$	100	2.3	6.1
	Col$_{h'}$ + Col$_h$–I + Col$_h$	108	2.5	6.5
	I + Col$_h$–I	127	0.6	1.5
9	Crys–Col$_h$	82	2.6	7.4
	Col$_h$–I	162	1.5	3.4
10	Crys–Crys′	40	6.3	20.1
	Crys′–Col$_h$	73	3.1	8.9
	Col$_h$–I	174	1.8	4.1
11	Crys–Col$_h$	38	80.8	259.8
	Col$_h$–I	174	1.8	4.0
12	Crys–Col$_h$	37	71.4	230.3
	Col$_h$–I	170	2.2	5.0
14	Crys–Crys′	50	40.9	126.4
	Crys′–Col$_h$	62	82.6	246.4
	Col$_h$–I	165	2.4	5.5

[a] Crys and Crys′: two crystalline phases of different thermodynamic stability; Col$_h$ and Col$_{h'}$: two immiscible hexagonal columnar phases with different degree of ordering.



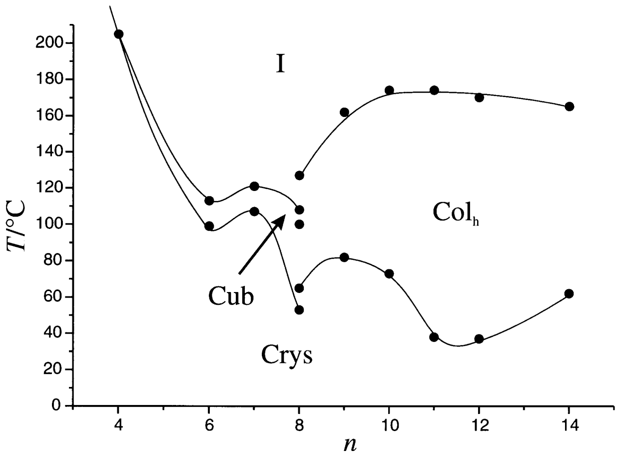


Fig. 5 Phase diagram for the complexes [AgSt(n-3,4,5)$_2$][OTf].

still no rational explanation so far for its occurence in the phase diagram.

However, the most remarkable feature of the mesomorphism of this homologue is that the biphasic behaviour described was observed on cooling from the isotropic liquid and on subsequent reheating cycles. This means that the species giving rise to the two sets of mesomorphism are somehow different, and that this difference is not 'annealed' out in the isotropic phase. What we know is that the 'as-prepared' and 'as-crystallised' complex gives an elemental analysis consistent with the formulation [AgSt(8-3,4,5)$_2$]-[OTf], and so the initial supposition is that the species can exist in more than one form, and these forms are not simply related as different crystal polymorphs. One possibility is that the complex could exist as a mixture of monomer and dimer. Recall that in the single crystal X-ray structure of [AgSt(1-4)$_2$][$C_8H_{17}OSO_3$], the complex was found to exist as a dimer with two silver complex cations being held together by bridging sulfate groups from the octyl sulfate chains.[28] It is conceivable that the triflate salts have a similar structure, and that a monomeric form can also exist. Thus, it is possible that the behaviour is explained by the presence of non-interconverting monomer and dimer.

The higher homologues ($n \geqslant 9$) behaved as typical hexacatenar mesogens do, in that they all showed an enantiotropic columnar phase, with large anisotropic domains, increasing from $n = 9$ to 11, and then decreasing for $n \geqslant 12$. Compounds with $n = 9$ to 12 did not recrystallise on cooling, and did not show a melting behaviour on subsequent heating. Similarly to the previous compounds showing anisotropic glasses, it was not possible to measure the ΔC_p and the T_g of the glass transition.

Discussion

Systems containing four flexible alkoxy chains

Four alkoxy chains in the positions 3 and 4. The complexes having this substitution pattern behave typically as tetracatenar mesogens, showing cubic and columnar phases, although N and S_C phases are not seen.[12a,b] Slight differences in the mesomorphism of the triflate and dodecyl sulfate salts were observed and while both showed enantiotropic cubic and columnar mesophases with a wide temperature range, the triflate salts had slightly higher transition temperatures.

However, the most important contrast is that in the triflate salts, the cubic phase appeared to longer chain length ($n = 7$ to 14) than in the related DOS salts ($n = 4$ to 10). This is explained by recalling that in the DOS salts, the alkyl sulfate chain adds to the curvature at the paraffinic/aromatic interface whereas in the triflate systems, this is not the case. Thus, for a given chain length on the stilbazole, the interfacial curvature will always be greater in the DOS salts, resulting in the onset of columar mesophases at shorter chain lengths. A related factor is likely to be due to the fact that mesophase formation is goverened by the interfacial curvature which, in turn, depends on the relative volumes of the core and the chains. In the triflate salts, not only does the anion not contribute to the aliphatic chain density, but in fact it can act to the opposite effect, increasing the volume of the core relative to the chains. Thus, phases with more strongly curved interfaces will require longer chain lengths.

That the triflate complexes are likely to be more ionic is supported by their higher melting points, but the fact that the clearing points of the two salts series are essentially the same points to the fact that the global breakdown in ionic interactions is not responsible for clearing, not inconsistent with a lattice melting model.[28]

By XRD and dilatometry,[11a] a linear variation of the lattice parameters and of the specific volume of both phases of the DOS series as a function of n was observed, even during the cross-over from one phase to the other. After deduction of the epitaxial relationships between the two mesophases, it was concluded that the transition Col-to-Cub occured with rather small structural changes, and a model based on undulated columns was proposed. In the case of the triflate compounds, preliminary X-ray results suggest a completely different mechanism, since an important jump in the variation of the lattice parameters of the two phases was recorded. The results of this study will be reported in due course.[29]

Interestingly, the cubic phase-to-isotropic liquid transition shows by DSC a fairly broad diffuse endotherm which may suggest a clearing process involving several steps. This peculiar phenomenom has been attributed by others to the breakdown of the molecular order of the cubic lattice.[30] This may further explain the supercooling observed on cooling of the isotropic liquid.

Four alkoxy chains in the positions 3 and 5. The difference in thermal behaviour as a function of the counter anion is more evident here, and clearly shows the crucial role of the dodecyl sulfate chain in stabilising mesophases. While only the tetradecyloxy homologue of the OTf series is mesomorphic showing a columnar phase, all members of the DOS series are mesomorphic for $n > 4$. As mentioned above, these complexes are virtually unique examples of mesomorphic 3,5-disubstituted tetracatenar materials with only four rings in the structure.[12a,b] For the DOS salts, the minimum requirement for mesomorphism (six methylene groups per chain) is probably linked to the absence of the alkoxy chains in the 4-position, that is a minimum volume of aliphatic chains is required to be able to generate an aliphatic matrix of sufficient density and in an *appropriate position* to stabilise the columns and to compensate the void created by the absence of chains in the 4-position.

This reinforces the important role of the DOS chain in the promotion of mesomorphism in these systems. Thus, on crossing the aromatic/paraffinic boundary, the DOS chain interacts sterically with the *meta* chains causing them to adopt a spatial disposition different to that in the triflate salts where no such steric interactions take place, as well as contributing positively to the interfacial curvature. Thus, we propose that in addition to enhancing the alkyl chain density, the DOS chain modifies the spatial distribution and allows the void of the 4-position chain to be more readily addressed. A test of this idea will be available when the X-ray data are considered as there should be no appreciable interdigitation of columns if this model is correct.

Four alkoxy chains in the positions 2 and 4. The complexes having this substitution pattern showed only monotropic behaviour, consisting of nematic and, in one case only, smectic C phases. It is likely that the destabilisation of the liquid-crystalline properties results from the alkoxy chain in the 2-position which, it is assumed, acts as an additional lateral group. This behaviour is consistent with that shown by some organic liquid crystals having one or two lateral chain(s), although in the latter, the nematic phases showed a higher thermodynamic stability than in the present situation.

Systems containing six flexible alkoxy chains

Six alkoxy chains in the positions 3, 4 and 5. Almost all the complexes having this substitution pattern showed a columnar phase typical for such systems, although it appeared at smaller values of n in the DOS salts ($n = 4$) than in the OTf salts ($n = 8$), indicating once more the positive effect of the dodecyl sulfate chains on the chain density and interfacial curvature. The melting points are also much lower in the former (28–53 °C) than in the latter (40–60 °C), although the phase exists over a much wider temperature in the triflate series because of higher clearing temperatures.

One particularly striking feature is the rather unsual thermal behaviour of the short homologues of the triflate salts

($n = 6, 7, 8$). Indeed, the cubic phase displayed by these homologues was not at all expected primarily owing the strong curvature at the interface generated by the three periphal alkoxy chains. However, recall the argument above which related the enhanced volume of the core of these complexes to the presence of the triflate anion. This argument is also consistent with the observation of cubic phases in these hexacatenar materials as the increased core volume will reduce the interfacial curvature increasing the likelihood of a cubic phase being seen.

Six alkoxy chains in the positions 2, 3, 4 and 2, 4, 5. In these systems, liquid-crystal properties were not expected because of the location of two chains in the positions 2 and 3/5. Lateral interactions were not favoured, as evidenced by the low transition temperatures, and the non-efficient packing of the chains, both reasons excluding mesomorphism.

Conclusions

New low-melting metallomesogens have been obtained by simple reaction of a silver fragment with various poly-substituted stilbazole ligands. Furthermore, the wide collection of substances herein prepared allowed us to be able to predict the liquid-crystalline properties, and thus to propose some structure–property relationships. Interestingly, the complexation of the non-mesomorphic ligands to some silver salts induced mesomorphism in many ligand/metal combinations, proving in this case, that the mesomorphism is not necessarily the result of molecular anisotropy itself, but depends on the molecular aggregation and on the shape of these aggregates. This highlights a very interesting analogy to lyotropic liquid crystals, and can allow speculation about a general description of liquid crystalline mesophases. It seems indeed clearer that similar principles of phase descriptions used in lyotropic systems can be used here.

In order to probe this analogy to lyotropic systems, we will study the effects of aliphatic apolar solvents on the mesomorphism of these silver(I) complexes, as several other groups have already done.[31] Preliminary results from simple contact preparations between some silver(I) compounds and dodecane look very promising, confirming the amphiphilic character of these complexes. In this case, they behave typically as the so-called amphotropic systems.[6a,19,32]

Experimental procedures

All the solvents were distilled prior to use according to standard procedures:[33] CH_2Cl_2 was distilled over calcium hydride, methanol from magnesium and iodine, tetrahydrofuran (THF) from sodium and benzophenone, toluene from sodium, acetone from potassium permanganate. Diethyl ether was dried and stored over sodium wire. 4-Methylpyridine was distilled from sodium hydroxide and stored over sodium hydroxide pellets. Potassium carbonate was kept in the oven. All other chemicals were used as supplied.

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ACL250 or AM400 spectrometer and referenced to external tetramethylsilane. The coupling constants were measured by the use of a program Window NMR (1D-Win NMR, Bruker, MS Window). One-bond ($^1J_{CH}$) and multiple-bond ($^2J_{CH}$, $^3J_{CH}$, and $^4J_{CH}$) C–H correlation spectra were recorded to allow a correct and full assignment of the proton and carbon peaks of all the substances. Microanalysis was performed by the University of Sheffield micro-analytical service. Infrared spectra were recorded on a Perkin–Elmer 684 spectrophotometer. The study of the thermal behaviour was achieved by DSC analysis, carried out using a Perkin–Elmer DSC7 instrument using various heating rates (2, 5 and 10 K min^{-1}) and the mesomorphism was studied by hot-stage, polarising microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller. All of the mesophases were characterised by their optical textures, and then confirmed by XRD. The spectroscopic and analytical data of all the intermediate substances (aldehydes, esters and alcohols) were good and in agreement with the proposed structures.

Preparation of the poly(alkoxy)benzaldehydes

2,4-Di-, 2,3,4-tri- and 2,4,5-tri-alkoxybenzaldehydes were synthesised as described previously, although for the trisubstituted benzaldehydes, pentan-2-one was prefered due to its higher boiling point, and the reaction was carried out under an inert atmosphere (N_2). Two equivalents of K_2CO_3 were systematically used per hydroxy group. They were obtained in good yields, ranging from 66 to 89%, and of analytical purity after purification by flash column chromatography (silica gel, CH_2Cl_2). IR(CsI/Nujol, cm^{-1}): 2,4-didecyloxybenzaldehyde: $\nu_{(C=O)}$ 1680s, $\nu_{(H-C=O)}$ 2715w; 2,3,4-trioctyloxybenzaldehyde: $\nu_{(C=O)}$ 1688s, $\nu_{(H-C=O)}$ 2730w; 2,4,5-trioctyloxybenzaldehyde: $\nu_{(C=O)}$ 1660s, $\nu_{(H-C=O)}$ 2730w.

3,5-Di and 3,4,5-tri-alkoxybenzaldehydes were obtained differently, and the preparation of one example is given. Methyl 3,5-dihydroxybenzoate (3.5 g, 20.2 mmol), K_2CO_3 (11.2 g, 81.0 mmol) and 1-bromooctane (8.7 g, 44.4 mmol) were placed in a flask filled with pentan-2-one (100 cm^3), and the reaction mixture was heated at reflux for 24 h. When cooled to room temperature, the mixture was filtered through a pad of Celite and the solvent evaporated under reduced pressure. The product was purified by column chromatography (SiO_2, CH_2Cl_2–hexane 4 : 1). The yield was 84% (6.7 g). All of the esters were purified similarly, and obtained in good yields ranging from 75 to 94%. IR(CsI/Nujol, cm^{-1}): $\nu_{(C=O)}$ 1730s, $\nu_{(C-OMe)}$ 1300m.

The reduction was carried out under an atmosphere of nitrogen. Methyl 3,5-dioctyloxybenzoate (6 g, 15.3 mmol) was dissolved in THF (50 cm^3), and $LiBH_4$ (0.83 g, 38.2 mmol) was added by portions to the solution; the mixture was heated at reflux for 1 h. Then, dry methanol (10 cm^3) was added dropwise to the refluxing mixture over a period of 1 h. The mixture was left 6 h at reflux and under vigorous stirring, and was then allowed to cool to room temperature. A solution of dilute HCl (20 cm^3, 3% v/v) was added until the pH was neutral. The alcohol was extracted in diethyl ether (2 × 250 cm^3), washed with water (2 × 200 cm^3), rinsed with brine (100 cm^3), and the organic layer was dried over $MgSO_4$. The solvents were removed under reduced pressure and the alcohol purified by flash-column chromatography (SiO_2, CH_2Cl_2–MeOH 99:1 to 90:10). The yield was effectively quantitative (97%, 5.4 g). All of the benzyl alcohols were purified similarly, and obtained in good yields ranging from 85 to 97%. IR(CsI/Nujol, cm^{-1}) $\nu_{(O-H)}$ 3340br, s.

The oxidation of the alcohols was carried out in the air and at room temperature. 3,5-Dioctyloxybenzyl alcohol (4 g, 11.0 mmol) was dissolved in CH_2Cl_2 (10 cm^3), and added to a suspension of pyridinium chlorochromate (3.6 g, 16.5 mmol) in CH_2Cl_2 (40 cm^3). The mixture immediately turned dark as the solution of alcohol was added, and was left stirred for 4 h. The product was directly recovered following filtration over a pad of silica gel and after evaporation of the solvent to give the aldehyde in good yield (85%, 3.4 g). When necessary, the aldehydes were once more purified by flash-column chromatography (SiO_2, CH_2Cl_2). All of the benzaldehydes were purified similarly, and obtained in good yields ranging from 70 to 95%. IR(CsI/Nujol, cm^{-1}): $\nu_{(C=O)}$ 1705s, $\nu_{(H-C=O)}$ 2710w.

Preparation of the poly(alkoxy)stilbazoles

The five new series of ligands were prepared and purified in the identical manner as the already given detailed procedure for the preparation of 3,4-dialkoxy-4-stilbazole.[11a] All the ligands were found to be analytically pure (Table 6), except for some homologues of the 3,5-disubstituted series which were found difficult to purify, and were used as such. Nevertheless, the structure of all the ligands were confirmed by NMR spectroscopy, for which no extra signals or impurities were observed. The NMR data of one derivative of each series are given below, and the C–H correlation spectra were made available to the referees. The lettering of the hydrogen and carbon atoms follows the same system as already used.[12c] The protons of the double bond (k, l) and those of the pyridine ring (n, o) were studied as a AB system and as a AA′XX′ system respectively.

Spectroscopic and analytical data for the ligands [St(*n*-*x*,*y*,*z*)]

St(6-3,5). δ_H(250.13 MHz, $CDCl_3$): 0.90 (a′, t, $^3J_{HH}$ 6.6 Hz, 6 H), 1.41 (b′, m, 12 H), 1.78 (c′, m, 4 H), 3.96 (d′, t, $^3J_{HH}$ 6.6 Hz, 4 H), 6.43 (e, t, $^4J_{eg}$ 2.3 Hz, 1 H), 6.67 (g, d, $^4J_{ge}$ 2.3 Hz, 2 H), 6.97 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 1 H), 7.27 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 1 H), 7.33 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.4 Hz, 2 H), 8.56 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.7 Hz, 2 H). δ_C(62.9 MHz, $CDCl_3$): 14.0 (a′), 22.6, 25.7, 29.2, 31.6 (b′, c′), 67.8 (d′), 101.9 (e), 105.6 (g), 120.9 (n), 126.3 (l), 133.3 (k), 137.9 (h), 144.5 (m), 150.1 (o), 160.6 (f).

St(7-2,4). δ_H(250.13 MHz, $CDCl_3$): 0.89, 0.90 (a, a″, 2 t, $^3J_{HH}$ 6.4 Hz, 6 H), 1.40 (b, b″, m, 16 H), 1.82 (c, c″, m, 4 H), 3.96, 3.99 (d, d″, 2 t, $^3J_{HH}$ 6.4 Hz, 4 H), 6.45 (f, d, $^4J_{fj}$ 2.0 Hz, 1 H), 6.49 (j, dd, $^3J_{ji}$ 8.5 Hz, $^4J_{jg}$ 2.0 Hz, 1 H), 6.95 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 1 H), 7.31 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.1 Hz, 2 H), 7.47 (i, d, $^3J_{ij}$ 8.5 Hz, 1 H), 7.58 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 1 H), 8.51 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.1 Hz, 2 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a″), 22.6, 26.0, 26.2, 29.1, 29.2, 29.3, 31.8 (b, b″, c, c″), 68.2, 68.5 (d, d″), 99.8 (f), 105.8 (j), 118.1 (h), 120.6 (n), 123.7 (l), 128.2 (i), 128.3 (k), 145.9 (m), 150.0 (o), 158.2 (g), 160.9 (e).

St(8-3,4,5). δ_H(250.13 MHz, $CDCl_3$): 0.96 (a, t, $^3J_{HH}$ 6.5 Hz, 3 H), 0.98 (a′, t, $^3J_{HH}$ 6.5 Hz, 6 H), 1.37 (b, b′, m, 30 H), 1.74 (c, c′, m, 6 H), 3.98 (d, t, $^3J_{HH}$ 6.5 Hz, 2 H), 4.02 (d′, t, $^3J_{HH}$ 6.5 Hz, 4 H), 6.72 (g, s, 2 H), 6.86 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 1 H), 7.19 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 1 H), 7.32 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.4 Hz, 2 H), 8.54 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.4 Hz, 2 H). δ_C(62.9 MHz, $CDCl_3$): 14.0 (a′), 14.1 (a), 22.6, 22.7, 25.8, 29.4, 29.7, 30.3, 31.6, 31.8 (b, b′, c, c′), 68.9 (d′), 73.5 (d), 105.7 (g), 120.8 (n), 124.8 (l), 131.3 (e), 133.4 (k), 139.2 (h), 144.8 (m), 150.1 (o), 153.4 (f).

St(8-2,3,4). δ_H(250.13 MHz, $CDCl_3$): 0.88, 0.90 (a, a′, a″, 2 t, $^3J_{HH}$ 6.7 Hz, 9 H), 1.39 (b, b′, b″, m, 30 H), 1.80 (c, c′, c″, m, 6 H), 3.97, 3.98, 4.04 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 6 H), 6.67 (j, d, $^3J_{ji}$ 9.0 Hz, 1 H), 6.90 (l, AB, $^{trans}J_{lk}$ 16.6 Hz, 1 H), 7.28 (i, d, $^3J_{ij}$ 9.0 Hz, 1 H), 7.32 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.4 Hz, 2 H), 7.58 (k, AB, $^{trans}J_{kl}$ 16.6 Hz, 1 H), 8.52 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.4 Hz, 2 H). δ_C(62.9 MHz, $CDCl_3$): 14.0, 14.1 (a, a′, a″), 22.6, 22.7, 25.8, 26.0, 29.3, 30.3, 30.4, 31.6, 31.7 (b, b′, b″, c, c′, c″), 68.8, 73.7, 74.3 (d, d′, d″), 108.6 (j), 120.6 (n), 120.9 (i), 123.2 (h), 124.4 (l), 128.1 (k), 141.9 (f), 145.5 (m), 150.0 (o), 151.8 (g), 154.1 (e).

St(8-2,4,5). δ_H(250.13 MHz, $CDCl_3$): 0.86, 0.88 (a, a′, a″, 2 t, $^3J_{HH}$ 6.7 Hz, 9 H), 1.38 (b, b′, b″, m, 30 H), 1.80 (c, c′, c″, m, 6 H), 3.97, 3.98, 4.00 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 6 H), 6.49 (f, s, 1 H), 6.87 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 1 H), 7.12 (i, s, 1 H), 7.32 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.1 Hz, 2 H), 7.61 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 1 H), 8.52 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.1 Hz, 2 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, a″), 22.7, 26.1, 26.3, 29.3, 29.4, 29.6, 31.8 (b, b′, b″, c, c′, c″), 69.3, 69.7, 70.7 (d, d′, d″), 100.4 (f), 113.5 (i), 117.5 (h), 120.6 (n), 123.6 (l), 127.9 (k), 143.3 (j), 145.7 (m), 150.0 (o), 151.3 (e), 152.4 (g).

Preparation of the silver complexes

The preparation of the silver(I) dodecyl sulfate was achieved as previously described.[11a] In the case of the silver(I) triflate com-

Table 6 Microanalytical data for the stilbazoles[a]

St(*n*-*x*,*y*,*z*)	Yield (%)	MP/°C	C	H	N
St(13-3,4)	89	89	80.7 (81.0)	11.1 (11.0)	2.3 (2.4)
St(14-3,4)	70	91	80.5 (81.3)	11.3 (11.1)	2.7 (2.3)
St(18-3,4)	78	94	81.2 (81.9)	12.0 (11.6)	1.8 (1.9)
St(1-3,5)	58	92	74.5 (74.7)	6.4 (6.3)	5.8 (5.8)
St(4-3,5)[b]	89	—	75.4 (77.5)	8.1 (8.4)	3.9 (4.3)
St(6-3,5)	80	36	78.1 (78.7)	9.2 (9.2)	4.0 (3.7)
St(7-3,5)	75	49	78.5 (79.2)	9.8 (9.6)	3.7 (3.4)
St(9-3,5)	62	55	79.5 (80.0)	10.3 (10.2)	2.8 (3.0)
St(11-3,5)	53	51	79.6 (80.6)	11.0 (10.6)	2.4 (2.7)
St(12-3,5)	86	55	79.8 (80.8)	10.9 (10.8)	2.7 (2.5)
St(14-3,5)	85	64	80.6 (81.3)	11.2 (11.1)	2.5 (2.3)
St(7-2,4)	40	64	78.9 (79.2)	9.8 (9.6)	3.3 (3.4)
St(10-2,4)	77	44	80.0 (80.3)	10.4 (10.4)	3.0 (2.8)
St(14-2,4)	82	55	81.3 (81.3)	11.4 (11.1)	2.3 (2.3)
St(1-3,4,5)	58	97	70.4 (70.8)	6.2 (6.3)	5.1 (5.2)
St(4-3,4,5)	67	64	75.7 (75.5)	9.0 (8.9)	3.5 (3.5)
St(5-3,4,5)[b]	85	—	76.5 (76.5)	9.5 (9.4)	3.2 (3.2)
St(6-3,4,5)[b]	90	—	76.6 (77.3)	9.8 (9.8)	2.7 (2.9)
St(7-3,4,5)	85	49	77.9 (78.0)	10.1 (10.2)	2.6 (2.7)
St(8-3,4,5)	86	48	78.6 (78.5)	10.7 (10.5)	2.5 (2.5)
St(9-3,4,5)	78	41	78.9 (79.0)	11.1 (10.8)	2.0 (2.3)
St(10-3,4,5)	82	44	79.6 (79.4)	11.1 (11.0)	2.1 (2.1)
St(11-3,4,5)	76	48	79.8 (79.8)	11.3 (11.2)	2.1 (2.0)
St(12-3,4,5)	66	51	79.9 (80.2)	11.3 (11.4)	1.7 (1.9)
St(14-3,4,5)	90	57	80.5 (80.7)	11.8 (11.7)	1.6 (1.7)
St(6-2,3,4)[b]	74	—	76.8 (77.3)	9.4 (9.8)	2.9 (2.9)
St(8-2,3,4)[b]	90	—	78.3 (78.5)	10.8 (10.5)	2.4 (2.5)
St(10-2,3,4)	76	41	79.6 (79.4)	11.0 (11.0)	2.4 (2.1)
St(12-2,3,4)	61	51	79.9 (80.2)	11.4 (11.4)	1.8 (1.9)
St(14-2,3,4)	89	63	80.8 (80.7)	11.8 (11.7)	1.4 (1.7)
St(8-2,4,5)	84	66	78.5 (78.5)	10.6 (10.5)	2.6 (2.5)
St(14-2,4,5)	86	65	80.3 (80.7)	12.0 (11.7)	1.4 (1.7)

[a] Calculated values in parentheses (%). [b] Obtained as oils.

plexes, the reactions were carried out in dry acetone. When cooled, the resulting yellow precipitate was filtered, crystallised from hot acetone (once or twice), recovered by filtration and dried under high vacuum. The complexes were obtained in satisfying yields, with good analytical purity (Tables 7 and 8). The NMR data (^{1}H, ^{13}C and ^{19}F) were in agreement with the expected structures, and are given below for one homolog of each series.

Spectroscopic and analytical data for the complexes [AgSt(*n*-*x*,*y*,*z*)$_2$][DOS]

[AgSt(6-3,5)$_2$][DOS]. δ_H(250.13 MHz, CDCl$_3$): 0.84 (s, t, $^3J_{HH}$ 6.7 Hz, 3 H), 0.91 (a′, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.34 (b′, r, m, 42 H), 1.67 (q, m, 2 H), 1.76 (c′, m, 8 H), 3.90 (d′, t, $^3J_{HH}$ 6.7 Hz, 8 H), 4.13 (p, t, $^3J_{HH}$ 6.7 Hz, 2 H), 6.41 (e, t, $^4J_{eg}$ 2.1 Hz, 2 H), 6.57 (g, d, $^4J_{ge}$ 2.1 Hz, 4 H), 6.87 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 2 H), 7.17 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 2 H), 7.39 (n, AA′XX′, $|J_{no} + J_{no'}|$ 6.4 Hz, 4 H), 8.69 (o, AA′XX′, $|J_{on} + J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, CDCl$_3$): 14.1 (a′, s), 22.7, 25.8, 26.1, 29.3, 29.5, 29.6, 29.7, 31.9 (b′, c′, r, q), 68.1 (p), 69.2 (d′), 102.6 (e), 105.7 (g), 121.7 (n), 124.6 (l), 135.8 (k), 137.1 (h), 146.9 (m), 151.8 (o), 160.5 (f).

[AgSt(7-2,4)$_2$][DOS]. δ_H(250.13 MHz, CDCl$_3$): 0.84 (s, t, $^3J_{HH}$ 6.7 Hz, 3 H), 0.89 (a, a″, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.35 (b, b″, r, m, 50 H), 1.67 (q, m, 2 H), 1.81 (c, c″, m, 8 H), 3.94 (d, d″, t, $^3J_{HH}$ 6.7 Hz, 8 H), 4.11 (p, t, $^3J_{HH}$ 6.7 Hz, 2 H), 6.39 (f, d, $^4J_{fj}$

Table 7 Microanalytical data for the AgDOS complexes[a]

Complex	*n*	Yield (%)	C	H	N	S
[AgSt(*n*-3,5)$_2$][DOS]	1	74	58.5 (58.9)	6.5 (6.5)	3.2 (3.3)	2.7 (3.7)
	4	28	63.1 (63.3)	7.8 (7.8)	2.8 (2.7)	3.2 (3.1)
	6	58	66.1 (65.5)	8.6 (8.4)	2.4 (2.5)	2.8 (2.8)
	7	38	66.7 (66.5)	8.5 (8.7)	2.4 (2.3)	2.8 (2.7)
	9	69	68.1 (68.1)	9.4 (9.2)	2.2 (2.1)	2.6 (2.5)
	12	51	70.2 (70.1)	9.8 (9.8)	1.9 (1.9)	2.4 (2.2)
	14	67	71.5 (71.2)	10.2 (10.1)	1.6 (1.8)	2.2 (2.0)
[AgSt(*n*-2,4)$_2$][DOS]	7	67	65.8 (66.5)	8.8 (8.7)	2.2 (2.3)	2.8 (2.7)
	14	74	71.1 (71.2)	10.2 (10.1)	1.7 (1.8)	2.0 (2.0)
[AgSt(*n*-3,4,5)$_2$][DOS]	1	76	57.6 (57.7)	6.5 (6.5)	3.0 (3.1)	3.5 (3.5)
	4	56	63.5 (63.7)	8.2 (8.2)	2.3 (2.4)	2.6 (2.7)
	5	15	65.6 (65.2)	8.9 (8.6)	2.4 (2.2)	2.6 (2.5)
	6	32	66.6 (66.5)	9.0 (9.0)	2.1 (2.1)	2.7 (2.4)
	7	68	67.4 (67.6)	9.3 (9.3)	2.2 (2.0)	2.4 (2.3)
	8	64	68.8 (68.6)	9.7 (9.6)	1.8 (1.9)	2.1 (2.1)
	9	51	69.4 (69.5)	10.0 (9.8)	1.9 (1.8)	2.1 (2.0)
	10	58	70.5 (70.3)	10.2 (10.1)	1.6 (1.7)	2.0 (1.9)
	11	55	71.3 (71.1)	9.5 (10.3)	2.0 (1.6)	1.8 (1.8)
	14	64	72.7 (72.9)	10.8 (10.8)	1.7 (1.4)	1.5 (1.6)
[AgSt(*n*-2,3,4)$_2$][DOS]	8	53	68.6 (68.6)	9.5 (9.6)	1.8 (1.9)	2.1 (2.1)
	14	79	73.4 (72.9)	10.9 (10.8)	1.4 (1.4)	1.4 (1.6)
[AgSt(*n*-2,4,5)$_2$][DOS]	8	52	68.6 (68.6)	9.7 (9.6)	1.8 (1.9)	2.2 (2.1)
	14	45	72.8 (72.9)	10.9 (10.8)	1.6 (1.4)	1.6 (1.6)

[a] Calculated values in parentheses (%).

Table 8 Microanalytical data for the AgOTf complexes[a]

Complex	*n*	Yield (%)	C	H	N	S
[AgSt(*n*-3,4)$_2$][OTf]	4	82	56.5 (59.6)	5.8 (6.0)	3.2 (3.1)	4.0 (3.5)
	6	88	59.6 (60.0)	6.9 (6.9)	2.8 (2.7)	3.7 (3.1)
	7	75	60.9 (61.4)	7.2 (7.3)	2.6 (2.6)	3.7 (3.0)
	8	80	61.8 (62.6)	7.7 (7.7)	2.8 (2.5)	2.7 (2.8)
	10	64	64.9 (64.7)	8.4 (8.3)	2.1 (2.2)	3.0 (2.6)
	12	94	66.4 (66.4)	8.6 (8.8)	1.9 (2.1)	2.7 (2.4)
	13	80	67.0 (67.2)	8.9 (9.0)	2.0 (2.0)	2.2 (2.3)
	14	89	67.4 (67.9)	9.5 (9.2)	1.9 (1.9)	2.4 (2.2)
	18	88	71.1 (70.2)	10.2 (9.9)	1.9 (1.6)	(1.9)
[AgSt(*n*-3,5)$_2$][OTf]	6	56	59.1 (60.0)	6.9 (6.9)	2.6 (2.7)	3.7 (3.1)
	9	66	63.4 (63.7)	8.1 (8.0)	2.6 (2.3)	2.9 (2.7)
	12	40	66.4 (66.4)	8.7 (8.8)	2.0 (2.1)	2.4 (2.4)
	14	79	67.6 (67.9)	9.3 (9.2)	1.7 (1.9)	2.8 (2.2)
[AgSt(*n*-2,4)$_2$][OTf]	7	61	61.3 (61.4)	7.4 (7.3)	2.8 (2.6)	3.3 (3.0)
	14	87	67.3 (67.9)	9.2 (9.2)	1.9 (1.9)	1.8 (2.2)
[AgSt(*n*-3,4,5)$_2$][OTf]	4	54	57.8 (58.2)	6.7 (6.7)	2.7 (2.7)	3.1 (3.0)
	6	50	61.7 (62.0)	7.6 (7.8)	2.3 (2.3)	2.9 (2.6)
	7	64	63.3 (63.5)	8.2 (8.2)	2.2 (2.1)	2.6 (2.5)
	8	80	64.7 (64.9)	8.6 (8.6)	2.0 (2.0)	2.7 (2.3)
	9	53	66.1 (66.0)	8.9 (8.9)	1.9 (1.9)	2.5 (2.2)
	10	51	66.8 (67.1)	9.1 (9.2)	1.7 (1.8)	2.3 (2.1)
	11	60	67.7 (68.1)	9.6 (9.5)	1.4 (1.7)	1.8 (1.9)
	12	61	68.3 (68.9)	9.5 (9.7)	1.6 (1.6)	1.9 (1.9)
	14	78	70.3 (70.4)	10.3 (10.1)	1.3 (1.5)	1.8 (1.7)
[AgSt(*n*-2,3,4)$_2$][OTf]	8	85	65.3 (64.9)	8.6 (8.6)	2.0 (2.0)	2.4 (2.3)
	14	92	69.6 (70.4)	10.4 (10.1)	1.6 (1.5)	1.8 (1.7)
[AgSt(*n*-2,4,5)$_2$][OTf]	8	75	64.4 (64.9)	8.7 (8.6)	2.0 (2.0)	2.5 (2.3)
	14	76	70.6 (70.4)	10.6 (10.1)	1.4 (1.5)	2.0 (1.7)

[a] Calculated values in parentheses (%).

2.1 Hz, 2 H), 6.41 (j, dd, $^3J_{ji}$ 8.3 Hz, $^4J_{jg}$ 2.1 Hz, 2 H), 6.87 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.33 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 7.38 (i, d, $^3J_{ij}$ 8.3 Hz, 2 H), 7.58 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.64 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a″, s), 22.6, 26.0, 26.1, 29.0, 29.1, 29.3, 29.5, 29.7, 31.8, 31.9 (b, b″, c, c″, r, q), 68.0 (p) 68.1, 68.4 (d, d″), 99.5 (f), 105.7 (j), 117.5 (h), 121.3 (n), 122.3 (l), 128.6 (i), 130.6 (k), 148.1 (m), 152.1 (o), 158.5 (g), 161.4 (e).

[AgSt(8-3,4,5)$_2$][DOS]. δ_H(250.13 MHz, $CDCl_3$): 0.84 (s, t, $^3J_{HH}$ 6.7 Hz, 3 H), 0.85 (a, t, $^3J_{HH}$ 6.4 Hz, 6 H), 0.88 (a′, t, $^3J_{HH}$ 6.4 Hz, 12 H), 1.35 (b, b′, r, m, 78 H), 1.67 (q, m, 2 H), 1.78 (c, c′, m, 12 H), 3.97 (d, t, $^3J_{HH}$ 6.4 Hz, 4 H), 3.98 (d′, t, $^3J_{HH}$ 6.4 Hz, 8 H), 4.09 (p, t, $^3J_{HH}$ 6.7 Hz, 2 H), 6.70 (g, s, 4 H), 6.81 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 2 H), 7.22 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 2 H), 7.42 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 8.67 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, s), 22.6, 22.7, 25.8, 26.1, 29.1, 29.3, 29.4, 30.4, 31.8, 31.9 (b, b′, c, c′, r, q), 68.1 (p), 69.2 (d′), 73.6 (d), 106.0 (g), 121.7 (n), 123.4 (l), 130.6 (e), 135.9 (k), 139.8 (h), 147.2 (m), 151.8 (o), 153.4 (f).

[AgSt(8-2,3,4)$_2$][DOS]. δ_H(250.13 MHz, $CDCl_3$): 0.85 (s, t, $^3J_{HH}$ 6.7 Hz, 3 H), 0.86, 0.87 (a, a′, a″, 2 t, $^3J_{HH}$ 6.7 Hz, 18 H), 1.35 (b, b′, b″, r, m, 78 H), 1.66 (q, m, 2 H), 1.80 (c, c′, c″, m, 12 H), 3.96, 3.97, 4.03 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 12 H), 4.10 (p, t, $^3J_{HH}$ 6.7 Hz, 2 H), 6.62 (j, d, $^3J_{ji}$ 8.7 Hz, 2 H), 6.86 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.22 (i, d, $^3J_{ij}$ 8.7 Hz, 2 H), 7.39 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 7.61 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.67 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, a″, s), 22.6, 26.0, 26.1, 26.2, 29.3, 29.4, 29.6, 29.7, 30.3, 31.8, 31.9 (b, b′, b″, c, c′, c″, r, q), 68.0 (p), 68.7, 73.7, 74.4 (d, d′, d″), 108.4 (j), 121.3 (i), 121.5 (n), 122.6 (h), 123.0 (l), 130.5 (k), 141.8 (f), 147.8 (m), 152.0 (o), 152.1 (g), 154.6 (e). Thermal data [T/°C (ΔH/kJ mol^{-1})]: $n = 8$, Crys • 98 (23) • I; $n = 14$, Crys • 41 (77) • Crys′ •52 (37) • I.

[AgSt(8-2,4,5)$_2$][DOS]. δ_H(250.13 MHz, $CDCl_3$): 0.84 (s, t, $^3J_{HH}$ 6.7 Hz, 3 H), 0.87, 0.88 (a, a′, a″, 2 t, $^3J_{HH}$ 6.7 Hz, 18 H), 1.35 (b, b′, b″, r, m, 78 H), 1.66 (q, m, 2 H), 1.82 (c, c′, c″, m, 12 H), 3.93, 3.94, 3.99 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 12 H), 4.10 (p, t, $^3J_{HH}$ 6.7 Hz, 2 H), 6.43 (f, s, 2 H), 6.83 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.06 (i, s, 2 H), 7.39 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.6 Hz, 4 H), 7.64 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.64 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.6 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, a″, s), 22.7, 26.0, 26.1, 26.2, 29.3, 29.4, 29.6, 29.7, 31.8 (b, b′, b″, c, c′, c″, r, q), 68.0 (p), 69.2, 69.5, 70.6 (d, d′, d″), 99.8 (f), 113.5 (i), 116.6 (h), 121.5 (n), 122.0 (l), 130.5 (k), 143.2 (j), 148.2 (m), 151.8 (o), 151.9 (e), 152.9 (g). Thermal data [T/°C (ΔH/kJ mol^{-1})]: $n = 8$, Crys • 88 (78) • I; $n = 14$, Crys • 64 (55) • Crys′ •78 (89) • I.

Spectroscopic and analytical data for the complexes [AgSt(n-x,y,z)$_2$][OTf]

[AgSt(7-3,4)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.90 (a, a′, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.40 (b, b′, m, 32 H), 1.81 (c, c′, m, 8 H), 3.94, 3.98 (d, d′, 2 t, $^3J_{HH}$ 6.7 Hz, 8 H), 6.69 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 6.71 (j, d, $^3J_{ji}$ 8.5 Hz, 2 H), 6.88 (i, dd, $^3J_{ji}$ 8.5 Hz, $^4J_{ig}$ 1.8 Hz, 2 H), 6.96 (g, d, $^4J_{ig}$ 1.8 Hz, 2 H), 7.18 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 7.29 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 8.56 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′), 22.7, 26.0, 29.2, 29.3, 31.9 (b, b′, c, c′), 69.0, 69.2 (d, d′), 111.5 (g), 113.0 (j), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.4 (n), 121.5 (i), 121.8 (l), 128.1 (h), 135.9 (k), 147.5 (m), 149.1 (e), 150.6 (f), 152.0 (o). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s).

[AgSt(6-3,5)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.89 (a′, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.34 (b′, m, 24 H), 1.75 (c′, m, 8 H), 3.86 (d′, t, $^3J_{HH}$ 6.7 Hz, 8 H), 6.38 (e, t, $^4J_{eg}$ 2.1 Hz, 2 H), 6.52 (g, d, $^4J_{ge}$ 2.1 Hz, 4 H), 6.81 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 2 H), 7.15 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 2 H), 7.33 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 8.59 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a′), 22.7, 26.1, 29.3, 29.5, 29.6, 31.9 (b′, c′), 68.1 (d′), 102.8 (e), 105.6 (g), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.9 (n), 124.3 (l), 136.2 (k), 136.9 (h), 147.3 (m), 152.0 (o), 160.5 (f). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s).

[AgSt(7-2,4)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.90 (a, a″, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.40 (b, b″, m, 32 H), 1.81 (c, c″, m, 8 H), 3.95, 3.96 (d, d″, 2 t, $^3J_{HH}$ 6.7 Hz, 8 H), 6.39 (f, d, $^4J_{fj}$ 2.1 Hz, 2 H), 6.41 (j, dd, $^3J_{ji}$ 8.3 Hz, $^4J_{jg}$ 2.1 Hz, 2 H), 6.88 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.35 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.7 Hz, 4 H), 7.37 (i, d, $^3J_{ij}$ 8.3 Hz, 2 H), 7.60 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.56 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a″), 22.6, 26.0, 26.1, 29.1, 29.3, 31.8, 31.9 (b, b″, c, c″), 68.2, 68.5 (d, d″), 99.6 (f), 105.8 (j), 117.4 (h), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.5 (n), 122.0 (l), 128.9 (i), 131.4 (k), 148.9 (m), 151.0 (o), 158.7 (g), 161.6 (e). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s).

[AgSt(7-3,4,5)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.88 (a, t, $^3J_{HH}$ 6.7 Hz, 6 H), 0.89 (a′, t, $^3J_{HH}$ 6.7 Hz, 12 H), 1.39 (b, b′, m, 48 H), 1.78 (c, c′, m, 12 H), 3.95 (d′, t, $^3J_{HH}$ 6.7 Hz, 8 H), 3.97 (d, t, $^3J_{HH}$ 6.7 Hz, 4 H), 6.67 (g, s, 4 H), 6.79 (l, AB, $^{trans}J_{lk}$ 16.2 Hz, 2 H), 7.21 (k, AB, $^{trans}J_{kl}$ 16.2 Hz, 2 H), 7.40 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 8.58 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′), 22.6, 26.1, 29.1, 29.3, 29.4, 30.4, 31.9 (b, b′, c, c′), 69.2 (d′), 73.6 (d), 105.9 (g), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.8 (n), 123.0 (l), 130.4 (e), 136.3 (k), 139.9 (h), 147.5 (m), 152.0 (o), 153.4 (f). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s).

[AgSt(8-2,3,4)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.85, 0.89 (a, a′, a″, 2 t, $^3J_{HH}$ 6.7 Hz, 18 H), 1.39 (b, b′, b″, m, 60 H), 1.78 (c, c′, c″, m, 12 H), 3.95, 3.96, 4.02 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 12 H), 6.56 (j, d, $^3J_{ji}$ 8.8 Hz, 2 H), 6.81 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.15 (i, d, $^3J_{ij}$ 8.8 Hz, 2 H), 7.33 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.7 Hz, 4 H), 7.59 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.59 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.7 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, a″), 22.7, 26.2, 29.3, 29.4, 29.5, 29.6, 30.4, 31.8, 31.9 (b, b′, b″, c, c′, c″), 68.7, 73.7, 74.4 (d, d′, d″), 108.4 (j), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.3 (i), 121.5 (n), 122.5 (h), 122.9 (l), 130.7 (k), 141.8 (f), 147.9 (m), 152.0 (o), 152.1 (g), 154.6 (e). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s). Thermal data [T/°C (ΔH/kJ mol^{-1})]: $n = 8$, Crys • 119 (24) • I; $n = 14$, Crys • 65 (44) • Crys′ •72 (27) • I.

[AgSt(8-2,4,5)$_2$][OTf]. δ_H(250.13 MHz, $CDCl_3$): 0.88, 0.89 (a, a′, a″, t, $^3J_{HH}$ 6.7 Hz, 18 H), 1.39 (b, b′, b″, m, 60 H), 1.81 (c, c′, c″, m, 12 H), 3.92, 3.93, 3.99 (d, d′, d″, 3 t, $^3J_{HH}$ 6.7 Hz, 12 H), 6.42 (f, s, 2 H), 6.83 (l, AB, $^{trans}J_{lk}$ 16.5 Hz, 2 H), 7.04 (i, s, 2 H), 7.39 (n, AA′XX′, $|J_{no}+J_{no'}|$ 6.4 Hz, 4 H), 7.64 (k, AB, $^{trans}J_{kl}$ 16.5 Hz, 2 H), 8.57 (o, AA′XX′, $|J_{on}+J_{on'}|$ 6.4 Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 14.1 (a, a′, a″), 22.7, 26.1, 26.2, 29.3, 29.4, 29.6, 31.8 (b, b′, b″, c, c′, c″), 69.2, 69.4, 70.6 (d, d′, d″), 99.7 (f), 113.5 (i), 116.4 (h), 120.8 (CF_3, q, J_{CF} 320 Hz), 121.5 (n), 121.6 (l), 130.8 (k), 143.2 (j), 148.6 (m), 151.9 (o), 152.0 (e), 152.9 (g). δ_F(235.36 MHz, $CDCl_3$): −78 (CF_3, s). Thermal data [T/°C (ΔH/kJ mol^{-1})]: $n = 8$, Crys • 58 (10) • Crys′ •110 (60) • I; $n = 14$, Crys • 67 (41) • Crys′ •80 (40) • I.

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