This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Polycatenar, bent-core pyridines and their discotic complexes with silver(I)

Deborah M. Huck[ab]; H. Loc Nguyen[a]; Bertrand Donnio[b]; Duncan W. Bruce Corresponding author[a]
[a] Department of Chemistry, University of Exeter, Exeter EX4 4QD, UK [b] CNRS-Université Louis Pasteur (UMR 7504), Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), Groupe des Matériaux Organiques (GMO), Institut de Physique et Chimie des Matériaux de Strasbourg, 67037 Strasbourg, France

Online publication date: 12 May 2010

To cite this Article Huck, Deborah M. , Nguyen, H. Loc , Donnio, Bertrand and Bruce Corresponding author, Duncan W.(2004) 'Polycatenar, bent-core pyridines and their discotic complexes with silver(I)', Liquid Crystals, 31: 4, 503 — 507
To link to this Article: DOI: 10.1080/02678290410001670566
URL: http://dx.doi.org/10.1080/02678290410001670566

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, VOL. 31, NO. 4, APRIL 2004, 503–507

Polycatenar, bent-core pyridines and their discotic complexes with silver(I)

DEBORAH M. HUCK†‡, H. LOC NGUYEN†, BERTRAND DONNIO‡ and
DUNCAN W. BRUCE*†

†Department of Chemistry, University of Exeter, Stocker Road,
Exeter EX4 4QD, UK
‡CNRS-Université Louis Pasteur (UMR 7504), Institut de Physique et Chimie
des Matériaux de Strasbourg (IPCMS), Groupe des Matériaux Organiques
(GMO), Institut de Physique et Chimie des Matériaux de Strasbourg, 23 Rue
des Loess, BP CR20, 67037 Strasbourg, France

(*Received 28 November 2003; accepted 16 January 2004*)

New, bent-core, polycatenar pyridine mesogens are described. Binding to silver(I) leads to complexes properly described as discotic.

Polycatenar mesogens [1] are generally considered as comprising an extended, more or less rigid core functionalized with three or more terminal chains. Interest in these materials arises as, despite the rod-like core, the mesomorphism of penta- and hexa-catenar derivatives is dominated by the formation of columnar phases. For tetracatenar derivatives where terminal substitution is in the 3,4-positions, the mesomorphism changes from that of rod-like mesogens at short chains lengths (N and SmC phases) to show columnar phases at longer chain lengths, occasionally through an intermediary cubic phase [2]. In almost all systems studied, the rigid core is effectively linear, but recently Swager and co-workers demonstrated examples based on 2,5-disubstituted thiophenes and hence showed that bent cores could be employed [3]. However, the bend in these systems is not too great, as evidenced by the fact that non-polycatenar derivatives showed mesophases characteristic of calamitic mesogens, rather than of bent-core systems [4].

We have devoted a good deal of attention to systems containing pyridine-based ligands from which have been generated mesomorphic materials via hydrogen bonding [5], halogen bonding [6] and complexation to metals from Groups 9, 10 and 11 [7, 8]. Our approach so far has used pyridines monosubstituted in the 2-, 3- [9] or 4-positions by styryl groups bearing between one and three alkoxy chains. However, the pyridines shown as **4** to **6** (see figure 1) differ from other reported systems in having a bent structure with a ‘bend angle’ of 120°, and as such are truly bent-core, polycatenar mesogens. Further, because they are based on a pyridine core, they offer the possibility of further functionalization through the ring nitrogen. We undertook the synthesis of these new materials and now report on their mesomorphism both as free ligands and when complexed to silver(I).

The benzylidene anilines **1** to **3** are obtained readily (figure 1) from the precursor benzaldehyde; under Siegrist conditions [10], the alkoxybenzylidene fragment is then transferred to the methyl groups of 3,5-lutidine to give pyridines **4** to **6**. All were obtained from the coupling reaction as colourless or off-white solids in yields of between 54 and 69% following purification by Soxhlet extraction (**4**) or column chromatography (**5** and **6**).

The two four-chained ligands, **4** and **5**, were not mesomorphic, melting directly to the isotropic state at 95 and 64°C, respectively and showed no signs of monotropic mesophase formation on cooling (see table 1). This is not entirely surprising, as the rigid core of the molecule is short when compared with most polycatenar and bent-core mesogens. However, the six-chained ligand **6** was mesomorphic and melted from the solid at 56°C to give a columnar phase which persisted only a few degrees to 60°C before clearing. Compound **6** also possesses a ‘short’ core and might not have been expected to be mesomorphic; but in this case we believe that it forms an anti-parallel arrangement which can fill space and form a columnar structure (see figure 2).

---

*Author for correspondence; e-mail: d.bruce@exeter.ac.uk

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001670566

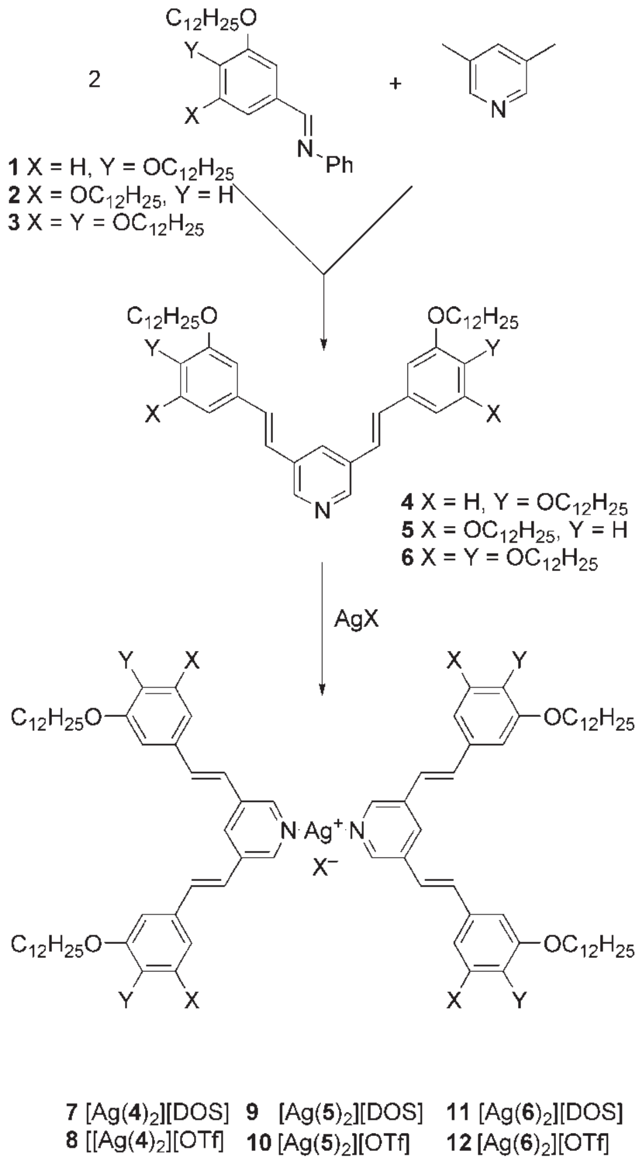


Figure 1. The ligands and complexes under study.

Such an arrangement is also analogous to that found in, for example, structurally similar $Ir(CO)_2$ complexes of hexacatenar β-diketonates described by Trzaska and Swager [11].

The pyridines were then complexed to AgDOS and AgOTf by stirring with the silver salt in CH_2Cl_2 at room temperature overnight in the dark and then crystallizing. The products were obtained as off-white solids in yields of between 68 and 89%. Although two of the precursor ligands were not mesomorphic, all of the new complexes showed columnar mesophases (see table 1).

Table 1. Mesomorphism of the new materials.

Compound	Transition	*T*/°C
4	Cr–I	95
5	Cr–I	64
6	Cr–Col$_h$	56
	Col$_h$–I	60
7	Cr–Col$_h$	68
	Col$_h$–I	183
8	Cr–Col$_h$	83
	Col$_h$–I^a	239
9	Cr–Col$_h$	48
	Col$_h$–I	123
10	Cr–Col$_h$	55
	Col$_h$–I	159
11	Cr–Col$_r$	60
	Col$_r$–I	131
12	Cr–Col$_r$	47
	Col$_r$–Col$_h$	113
	Col$_h$–I	185

[a] With decomposition.

Thus, while ligand **4** melted at 95°C, its complexes with both silver salts melted at lower temperatures giving way to columnar mesophases. With AgDOS (**7**), melting led to a columnar phase which persisted to 183°C, whereupon it cleared; with AgOTf (**8**), a columnar phase also formed and persisted to 239°C where it cleared. A similar story was found for complexes of **5** where a columnar phase was seen for both the DOS salt (**9**) and the triflate (**10**). Melting points were again below those of the ligand, while clearing points were in excess of 100°C although appreciably lower than those of complexes derived from **4**. On complexation of ligand **6**, the mesomorphic behaviour of the ligand was enhanced and with AgDOS (**11**) a columnar phase was seen from 60 to 131°C; when

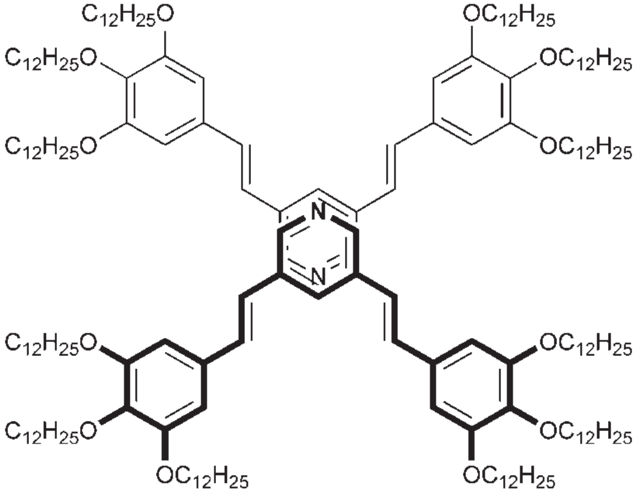


Figure 2. Proposed molecular arrangement in the columnar phase of **6**.

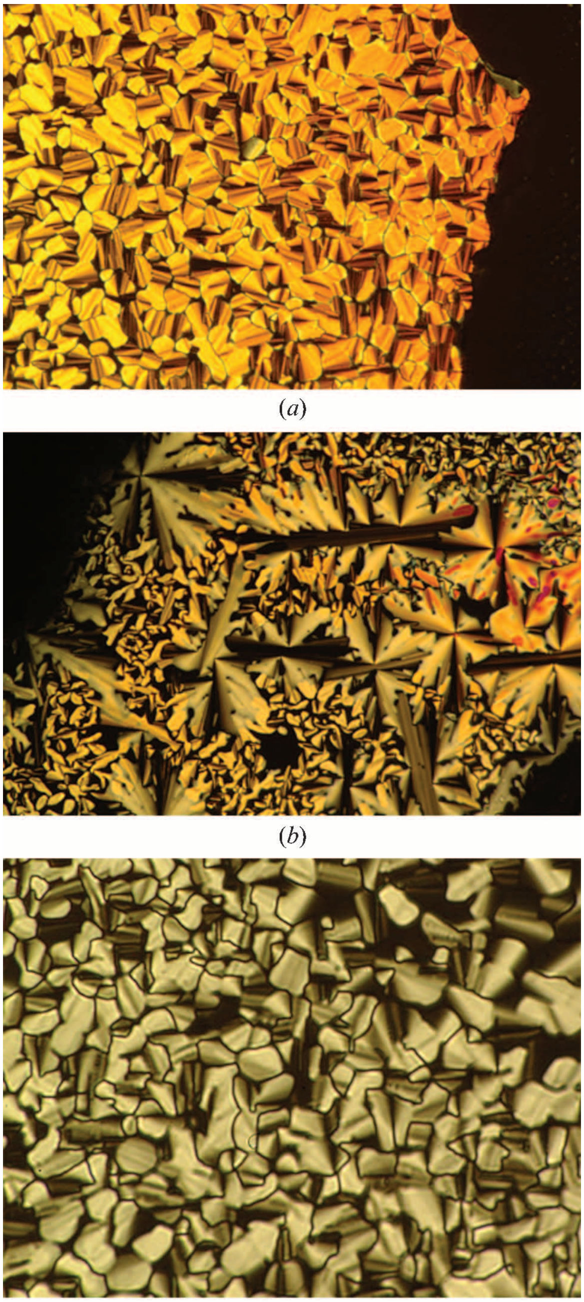
complexed to AgOTf (**12**), two columnar phases were seen, one exisiting between the melting point of 47 and 113°C, while the higher temperature phase persisted to the clearing point of 185°C.

That the complexes formed columnar phases was seen readily by optical microscopy, but it was necessary to use X-ray diffraction to determine the symmetry of the phases. Thus, it was found that all complexes **7–10** and **12** showed a $\mathrm{Col_h}$ phase as evidenced by the observation of (1 0), (1 1), (2 0) and, occasionally, (2 1) reflections along with reflections corresponding to a 4.5 Å spacing, characteristic of molten alkyl chains. Compound **12** showed an additional phase below the $\mathrm{Col_h}$ phase, which was identified as $\mathrm{Col_r}$ with *c*2*mm* symmetry—reflections were seen corresponding to the Miller indices (1 1), (2 0) and (3 1), (4 0), (2 2) and (1 3)—while the single mesophase of compound **11** was also $\mathrm{Col_r}$, again with *c*2*mm* symmetry. Optical textures representative of the $\mathrm{Col_h}$ and $\mathrm{Col_r}$ phases are shown in figure 3.

That all of the complexes were mesomorphic is perhaps understood readily, as figure 1 shows that when bound to silver, the complexes are classically discotic and, therefore, are able to stack one upon another. Thus, complexation has acted to turn these bent-core, polycatenar mesogens into components of discotic materials. However, while all the ligands melted or cleared below 100°C, the complexes were mesomorphic over an extended temperature range with, in general, triflates showing higher clearing temperatures than the dodecylsulfates, in line with observations we have made previously [7]. That the mesomorphic ranges are wider in the complexes than in the free ligands parallels the behaviour we have found previously for simpler stilbazoles [7], and undoubtedly the greater structural anisotropy consequent on complexation is a significant factor, while the flexible anion chain of the DOS salts again plays a rôle in destabilizing the mesophases compared with triflate. The higher mesophase stability may well be due to the presence of intermolecular electrostatic interactions caused by the presence of the silver cation and DOS or OTF anion.

Representative experimental details are now given; other compounds were made by directly analogous procedures. X-ray data were recorded as described previously [12]; other instrumental methods are as described in previous publications, for example reference [9]. Elemental analysis results are given in table 2.

3,4,5-Tridodecyloxybenzylidene aniline. 3,4,5-Tridodecyloxybenzaldehyde [13] (6.0 g, 9.1 mmol) was heated with stirring in ethanol (200 $\mathrm{cm^3}$) until it dissolved. Aniline (0.77 g, 8.27 mmol) was then added, followed by a few crystals of *p*-toluenesulfonic acid. The mixture was stirred and was allowed to cool to room temperature; as it did so a thick, white precipitate formed. The mixture was stirred for a further 2 h and the white precipitate was then filtered off and dried in a dessicator (8.23 g, 7.1 mmol, 88% yield). It was used without further purification.


(*a*)

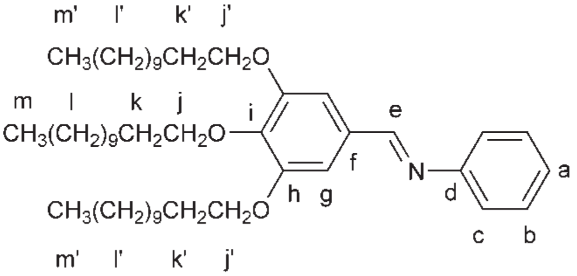
(*b*)

(*c*)

Figure 3. Optical textures: (*a*) the $\mathrm{Col_h}$ phase of **8** on cooling at 190°C, (*b*) the fern texture of the $\mathrm{Col_h}$ phase of **10** on cooling at 151°C, (*c*) the $\mathrm{Col_r}$ texture of **11** at 96°C on cooling.

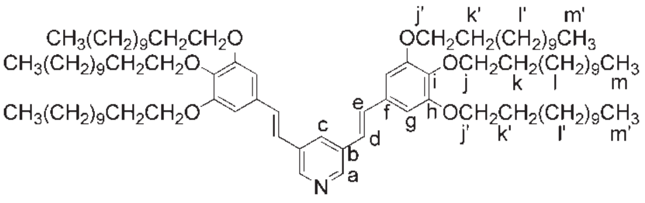
Table 2. Elemental analysis data for the new materials.

Compound	Yield/%	Calculated (found)/% C	H	N
1	91	80.8 (80.8)	10.8 (10.9)	2.9 (2.7)
2	98	80.8 (80.2)	10.8 (10.7)	2.6 (2.3)
3	88	80.2 (80.0)	11.4 (11.3)	1.9 (1.9)
4	69	81.2 (81.1)	11.2 (11.7)	1.4 (1.1)
5	54	81.2 (80.8)	11.2 (11.8)	1.4 (1.2)
6	62	80.4 (80.3)	11.7 (11.5)	1.0 (0.8)
7	68	74.6 (73.4)	10.5 (10.8)	1.2 (0.9)
8	89	72.6 (71.9)	9.9 (10.4)	1.2 (0.9)
9	86	74.6 (73.3)	10.5 (11.3)	1.2 (0.9)
10	75	72.6 (72.6)	9.9 (10.8)	1.2 (1.0)
11	76	75.5 (75.4)	11.1 (11.7)	0.9 (0.6)
12	85	74.0 (74.0)	10.7 (11.7)	0.9 (0.6)



^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.36$ (1H, s, He), 7.43 (2H, A_2B_2B', Hb, $^3J_{HH} = 7.77$ Hz), 7.26 (1H, A_2B_2B', Ha, $^3J_{HH} = 7.77$ Hz), 7.22 (2H, A_2B_2B', Hc, $^3J_{HH} = 7.77$ Hz), 7.17 (2H, s, Hg) 4.08 (4H, t, Hj′, $^3J_{HH} = 6.51$ Hz), 4.04 (2H, t, Hj, $^3J_{HH} = 6.51$ Hz), 1.86 (4H, m, Hk′), 1.77 (2H, m, Hk), 1.44 (54H, m, Hl, Hl′), 0.91 (9H, 2×t, Hm, Hm′, $^3J_{HH} = 6.96$ Hz). ^{13}C NMR (100.61 MHz, CD_2Cl_2): $\delta = 160.3$ (e), 153.8 (h), 152.6 (d), 141.5 (i), 131.79 (f), 129.5 (b), 126.0 (a), 121.1 (c), 107.2 (g), 73.8 (j), 69.5 (j′), 32.3, 30.8, 30.2, 30.1, 30.1, 30.0, 29.8, 29.7, 26.5, 23.1 (k, k′, l, l′), 14.3 (m, m).

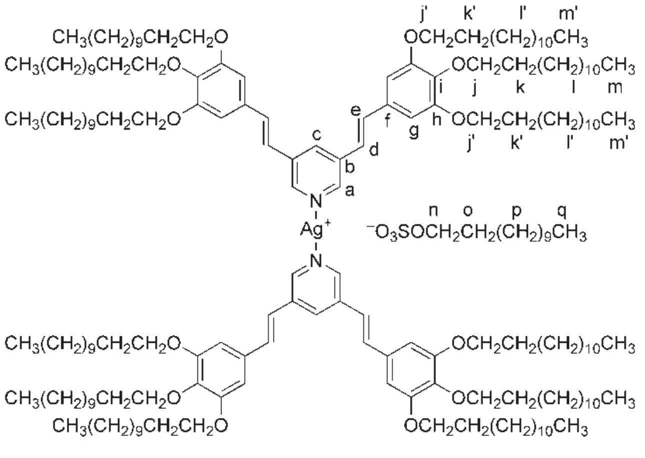
3′,5′-Di(3,4,5-tridodecyloxystyryl)pyridine. *N*-Phenyl-3,4,5-tridodecyloxybenzaldimine (3.0 g, 4.1 mmol) was dissolved in DMF (20 cm^3) on heating to 50°C. 3,5-Lutidine (0.21 g, 2.0 mmol) was added and the system was flushed with N_2. Potassium-*t*-butoxide (1.9 g, 15.6 mmol) was added in portions and the solution became dark red. The system was flushed again with N_2 and heated at 80°C with stirring for 2.5 h. After cooling the solution, HCl (10% solution) was added until pH 7. Distilled water (100 cm^3) was added follow by CH_2Cl_2 (150 cm^3). The organic phase was separated and washed with $NaHCO_3$ saturated solution (100 cm^3) and water (100 cm^3). After drying over Na_2SO_4 the solvent was removed *in vacuo*. The product was purified by column chromatography on silica gel with ether/hexane (3/7). A few drops of triethylamine were added to the solvent system to prevent the product from sticking to the column.



^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.58$ (2H, d, Ha, $^4J_{HH} = 2.03$ Hz), 7.93 (1H, t (broad), Hc), 7.13 (2H, AB, He, $J = 16.24$ Hz), 6.97 (2H, AB, Hd, $J = 16.24$ Hz), 6.75 (4H, s, Hg), 4.05 (8H, t, Hj′, $^3J_{HH} = 6.25$ Hz), 4.00 (4H, t, Hj, $^3J_{HH}$, 6.57 Hz), 1.85 (8H, m, Hk′), 1.41 (108H, m, Hl, Hl′), 0.89 (12H, m, Hm, Hm′). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 153.4$ (h), 146.5 (a), 138.9 (f), 133.1 (b), 131.7 (e), 131.4 (i), 129.3 (c), 123.5 (d), 105.3 (g), 73.6 (j), 69.2 (j′), 32.0, 29.8, 29.7, 29.6, 29.4, 26.1, 22.7 (k, k′, l, l′), 14.1 (m, m′).

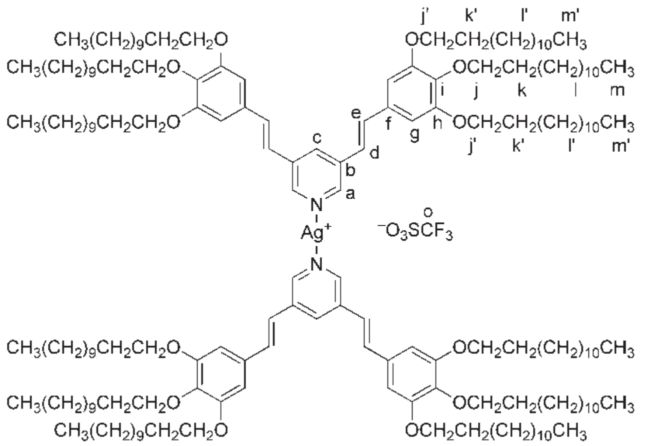
Bis[3′,5′-di(3,4,5-tridodecyloxystyryl)pyridine]silver(I) dodecylsulfate. 3′,5′-Di(3,4,5-tridodecyloxystyryl)pyridine (320 mg, 0.23 mmol) dissolved in CH_2Cl_2 (10 cm^3) was slowly added to a suspension of silver(I) dodecylsulfate (40 mg, 0.11 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred at room temperature for 15 h in the dark. It was then filtered through celite and the solvent was removed *in vacuo*. The product was stirred in hot acetone, the unreacted ligand dissolved and the remaining solid was filtered off, dissolved in CH_2Cl_2 and was precipitated by slow mixing with MeOH. The colourless solid product (263 mg, 0.08 mmol, 76% yield) was dried under vacuum.

Complex **7** was prepared similarly, but was less soluble in CH_2Cl_2 and so on completion of the reaction, the solvent was removed *in vacuo*. The residue was then dissolved in chloroform, filtered through celite and then purified in the same way as described for complex **11**.



^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.68$ (4H, d, Ha, $^4J_{HH} = 1.67$ Hz), 8.01 (2H, t (broad), Hc), 7.19 (4H, AB, He, $J = 16.32$ Hz), 6.93 (4H, AB, Hd, $J = 16.32$ Hz), 6.74 (8H, s, Hg), 4.10 (2H, t, Hn, $^3J_{HH} = 6.90$ Hz), 4.02 (16H, t, Hj′, $^3J_{HH} = 6.41$ Hz), 3.99 (8H, t, Hj, $^3J_{HH} = 6.51$ Hz), 1.80 (24H, m, Hk, Hk′), 1.45 (220H, m, Hl, Hl′, Ho, Hp), 0.89 (27H, t, Hm, Hm′, Hq, $^3J_{HH} = 6.58$ Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 153.4$ (h), 147.7 (a), 139.1 (b), 134.7 (i), 132.9 (e), 131.3 (f), 131.0 (c), 122.1 (d), 105.4 (g), 73.6 (j), 69.2 (j′), 68.3 (n), 32.0, 31.9, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 26.2, 25.9, 22.7 (k. k′, l, l′, o, p), 14.1 (m, m′, q).

Bis[3′,5′-di(3,4,5-tridodecyloxystyryl)pyridine]silver(I) triflate. Silver(I) triflate (23 mg, 0.09 mmol) was placed in a flask protected from light, to this 3′,5′-di(3,4,5-tridodecyloxystyryl)pyridine (250 mg, 0.18 mmol) dissolved in DCM (10 cm^3) was added slowly. The mixture was stirred at room temperature for 15 h. It was then filtered through celite and the solvent removed. The product was then dissolved in DCM and precipitated by slow mixing with MeOH. The off-white product (220 mg, 0.07 mmol, 85% yield) was dried under vacuum.



^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.61$ (4H, d (broad), Ha), 8.05 (2H, t (broad), Hc), 7.17 (4H, AB, He, $J = 16.56$ Hz), 6.89 (4H, AB, Hd, $J = 16.56$ Hz), 6.74 (8H, s, Hg), 4.00 (16H, t, Hj′, $^3J_{HH} = 6.42$ Hz), 3.99 (8H, t, Hj, $^3J_{HH} = 6.40$ Hz), 1.78 (24H, m, Hk, Hk′), 1.38 (216H, m, Hl), 0.89 (36H, m, Hm, Hm′). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 153.3$ (h), 147.5 (a), 138.8 (b), 134.8 (i), 133.0 (e), 131.5 (c), 131.2 (f), 122.7 (o), 121.7 (d), 105.1 (g), 73.5 (j), 68.9 (j′), 32.0, 31.8, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.7, 22.6 (k, k′, l, l′), 14.2 (m, m′).

This work was supported by the UK EPSRC (D.M.H. and H.L.N.) and the Collège Doctoral Européan de Strasbourg (D.M.H.). Helpful discussions with Dr Daniel Guillon (IPCMS, Strasbourg) are acknowledged gratefully.

References

[1] MALTHÊTE, J., NGUYEN, H.-T., and DESTRADE, C., 1993, *Liq. Cryst.*, **13,** 171; NGUYEN, H.-T., DESTRADE, C., and MALTHÊTE, J., 1997, *Adv. Mater.*, **9,** 375.

[2] FAZIO, D., MONGIN, C., DONNIO, B., GALERNE, Y., GUILLON, D., and BRUCE, D. W., 2001, *J. mater. Chem.*, **11,** 2852; ROWE, K. E., and BRUCE, D. W. 1998, *J. mater. Chem.*, **8,** 331.

[3] LEVITSKY, I. A., KISHIKAWA, K., EICHHORN, S. H., and SWAGER, T. M., 2000, *J. Am. chem. Soc.*, **122,** 2474; EICHHORN, S. H., PARASKOS, A. J., KISHIKAWA, K., and SWAGER, T. M., 2002, *J. Am. chem. Soc.*, **124,** 12 742; PARASKOS, A. J., and SWAGER, T. M., 2002, *Chem. Mater*. **14,** 4543.

[4] PELTZ, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mater.*, **11,** 707.

[5] See, e.g., WILLIS, K., PRICE, D. J., ADAMS, H., UNGAR, G., and BRUCE, D. W., 1995, *J. mater. Chem.*, **5,** 2195; PRICE, D. W., WILLIS, K., RICHARDSON, T., UNGAR G., and BRUCE, D. W., 1997, *J. mater. Chem.*, **7,** 883.

[6] NGUYEN, H. L., HORTON, P. N., HURSTHOUSE, M. B., LEGON, A. C., and BRUCE, D. W., 2004, *J. Am. chem. Soc.*, **126,** 16.

[7] BRUCE, D. W., 2000, *Acc. chem. Res.*, **33,** 831.

[8] BRUCE, D. W., 2001, *Adv. inorg. Chem.*, **52,** 151.

[9] HUCK, D. M., NGUYEN, H.-L., COLES, S. J., HURSTHOUSE, M. B., DONNIO, B., and BRUCE, D. W., 2002, *J. mater. Chem.*, **12,** 2879.

[10] SIEGRIST, A. E., 1967, *Helv. chim. Acta*, **50,** 1399.

[11] TRZASKA, S. T., and SWAGER, T. M., 1998, *Chem. Mater.*, **10,** 438.

[12] MORALE, F., DATE, R. W., GUILLON, D., BRUCE, D. W., FINN, R. L., WILSON, C., BLAKE, A. J., SCHRÖDER, M., and DONNIO, B., 2003, *Chem. Eur. J.*, **9,** 2484.

[13] DONNIO, B., and BRUCE, D. W., 1999, *New J. Chem.*, **23,** 275.