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*The synthesis and characterization of novel ionic liquid crystals displaying columnar mesomorphism induced upon complexation of 2,2′-bipyridine-4,4′-disubstituted ligands (**L**^{n}) are reported. A tetracoordination around the silver(**I**) centre has been obtained for the first time in metallomesogens based on chelated bipyridine ligands. The molecular organization in the mesophase for these [**Ag**(**L**^{n})$_2$][**OTf**] derivatives is strongly dependent on the coordination and ionic bonds which drive the supramolecular assembly.*

Keywords: 2,2′-bipyridines; metallomesogens; silver(***I***); triflate

INTRODUCTION

Self-assembly of liquid crystals, through inter or intramolecular interactions of different nature (hydrogen bonds, ionic interactions, dipole interactions), is a current approach to get new functional materials [1]. If the self-assembly is driven by the coordination chemistry is possible to give rise to metallomesogenic species with a variety of new architectures and properties [2–5]. For example, the 2,2′-bipyridine

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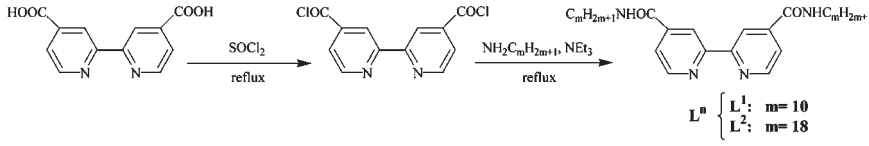
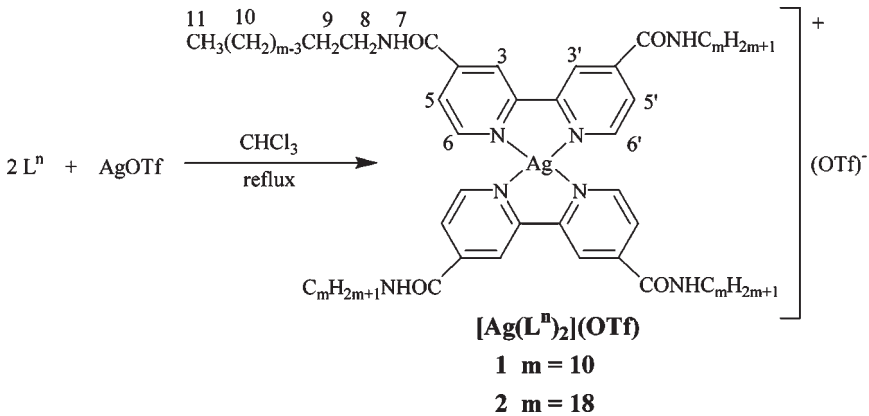


SCHEME 1 Synthetic route to the $\mathbf{L^n}$ ligands.

ligands, which are versatile building blocks for coordination compounds with interesting supramolecular applications [6], can be used also to give, through chelation, coordination complexes with mesomorphic properties [7]. Complexes based on two substituted 2,2′-bipyridine units usually display nematic or lamellar mesophases [4] while a columnar mesomorphism is showed only by polycatenar bipyridine-based species [8].

In this context we aimed to develop a strategy for the construction of supramolecular species by combining covalent and non covalent interactions. In particular we sought to design, starting from disubstituted bipyridines, four-chained complexes able to induce mesomorphic molecular edificies such as columns. In the present paper we report on the synthesis and characterization of two novel 2,2′-bypiridine ligands functionalized with amidic substituents in 4,4′-position, $\mathbf{L^n}$ (Scheme 1). The reaction of the $\mathbf{L^n}$ ligands with silver(**I**) triflate (AgOTf) afforded to ionic bis-chelated silver complexes [$\mathbf{Ag(L^n)_2}$][**OTf**], **1** and **2** (Scheme 2) whose columnar mesomorphism will be herein discussed.



SCHEME 2 Synthetic route to the [$\mathbf{(L^n)_2Ag}$][**OTf**] complexes and related proton numbering scheme.

EXPERIMENTAL

Materials and Measurements

The commercially available chemicals, used without further purification, are the following: 4,4′-dimethyl-2,2′-dipyridyl 99% (Aldrich); decylamine 99% (Fluka); octadecylamine 97% (Aldrich); triethylamine 99% (Aldrich); silver triflate 99% (Aldrich).

4,4′-Dicarboxy-2,2′-bipyridine and the corresponding dichloride were prepared following the methods previously described [9]. The ^{1}H NMR spectra were collected on a Bruker Avance DRX-300 spectrometer in $CDCl_3$ solution, with TMS as internal standard, IR spectra on a Spectrum One FT-IR Perkin Elmer spectrometer, as KBr disks. Elemental analyses were carried out with a Perkin-Elmer 2400 analyzer. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam CO 600 heating stage. The transition temperatures and enthalpies were measured on a Perkin-Elmer DSC 6 Differential Scanning Calorimeter with a heating and cooling rate of 10°C/min. The apparatus was calibrated with indium. Two or more heating/cooling cycles were performed on each sample. The powder X-ray diffraction patterns were obtained by using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with CuKα radiation; the high sensitive area detector was placed at a distance from the sample of 20 cm and at an angle $2\theta_D$ of 12°. CalCTec (Italy) heating stage is used as variable temperature device. The samples were heated at a rate of 5.0°C min^{-1} to the appropriate temperature. Measurements were performed by charging samples in Lindemann capillary tubes with inner diameter of 0.05 mm.

SYNTHESIS

Ligands L^n

2,2′-Bipyridine-4,4′-bis-(n-decylamide), L^1

A mixture of 2,2′-bipyridyl-4,4′-dicarbonyl chloride (0.288 g, 1.02 mmol), n-decylamine (0.386 g, 0.79 mL, 2.46 mmol) and triethylamine (0.207 g, 0.29 mL, 2.05 mmol) in toluene (30 mL), was refluxed under N_2, for 24 h. The crude product was collected by filtration and recrystallized from DMF/diethyl ether, to give the ligand $\mathbf{L^1}$ as a white solid (0.382 g; yield 71%). M.p. 255°C. Anal. Calcd. for $C_{32}H_{50}N_4O_2$ (522.77): C, 73.52; H, 9.64; N, 10.72. Found: C, 73.59; H, 9.69; N 10.92. IR (KBr): ν_{N-H} 3310 cm^{-1}(s), $\nu_{C=O}$ 1633 cm^{-1}(s).

TABLE 1 Optical and Thermal Data

Compound	Transition[a]	T/°C[b]	ΔH/kJ mol^{-1}
$\mathbf{L^2}$	Cr–Cr′	108.3	2.4
	Cr′–SmC	143.9	22.6
	SmC–I	213.6	48.2
	I–SmC	210.0	47.5
	SmC–Cr′	152.1	13.8
	Cr′–Cr	110.9	2.5
[$(\mathbf{L^1})_2$**Ag**][**OTf**] **1**	Cr–Col_r	138.9	0.2
	Col_r–I	178.6	3.6
	I–Col_r	175.3	3.6
	Col_r–Cr	135.0	0.2
[$(\mathbf{L^2})_2$**Ag**][**OTf**] **2**	Cr–Cr′	73.3	16.7
	Cr′–Cr″	108.5	7.0
	Cr″–Col_h	117.5	7.9
	Col_h–I_{dec}	299.0[c]	/

[a]Cr: crystal; Col_r: columnar rectangular; Col_h: columnar hexagonal; I: isotropic liquid. [b]Temperature data as peak onset. [c]Optical data.

2,2′-Bipyridine-4,4′-bis-(n-octadecylamide), L^2

This ligand was prepared by the above procedure using the n-octadecylamine. White solid (0.760 g, yield 60%). Thermotropic behaviour in Table 1. Anal. Calcd. for $C_{48}H_{82}N_4O_2$ (747.20): C, 77.16; H, 11.06; N, 7.50. Found: C, 76.96; H, 10.99; N, 7.46. IR (KBr): ν_{N-H} 3319 cm^{-1}(s), $\nu_{C=O}$ 1634 cm^{-1}(s).

Complexes [Ag(L^n)$_2$][OTF]

[Ag(L^1)$_2$][OTf], 1

A mixture of $\mathbf{L^1}$ (0.08 g, 0.15 mmol) and AgOTf (0.018 g, 0.075 mmol) in $CHCl_3$ (20 mL), was refluxed in the dark, under N_2, for 24 h. The resulting pale yellow solution was filtered through Celite and hexane was added to give the complex as a pale yellow solid (0.096 g, yield 95%). Thermotropic behaviour in Table 1. Anal. Calcd. for $C_{65}H_{100}AgF_3N_8O_7S$ (1300.64): C, 59.97; H, 7.75; N, 8.61. Found: C, 59.70; H, 7.65; N, 8.65. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (8H, br s, $H^{6,6'}$, $H^{7,7'}$); 8.02 (4H, s, $H^{3,3'}$); 7.68 (4H, d, $J = 4.3$ Hz, $H^{5,5'}$); 3.42 (8H, m, $H^{8,8'}$); 1.68 (8H, m, $H^{9,9'}$); 1.32 (56H, m, $H^{10,10'}$); 0.90 (12H, t, $J = 6.5$ Hz, $H^{11,11'}$); IR (KBr): ν_{N-H} 3308 cm^{-1}; $\nu_{C=O}$ 1634 cm^{-1}; ν_{OTf} 1252 cm^{-1}.

[Ag(L^2)$_2$][OTf], 2

This complex was prepared according to the procedure described for the complex **1**. White solid (0.066 g, yield 50%). Thermotropic

behaviour in Table 1. Anal. Calcd. for $C_{97}H_{164}AgF_3N_8O_7S$ (1749.14): C, 66.55; H, 9.45; N, 6.40. Found: C, 66.75; H, 9.52; N 6.30; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (8H, br s, $H^{6,6'}$, $H^{7,7'}$); 8.02 (4H, s, $H^{3,3'}$); 7.77 (4H, d, $J = 4.3$ Hz, $H^{5,5'}$); 3.45 (8H, m, $H^{8,8'}$); 1.68 (8H, m, $H^{9,9'}$); 1.29 (120 H, m, $H^{10,10'}$); 0.89 (12H, t, $J = 6.5$ Hz, $H^{11,11'}$); IR (KBr): ν_{N-H} 3315 cm^{-1}; $\nu_{C=O}$ 1634 cm^{-1}; ν_{OTf} 1250 cm^{-1}.

RESULTS AND DISCUSSION

The 2,2′-bipyridine-4,4′-diamide ligands $\mathbf{L^n}$, in which the number of carbon atoms in the aliphatic chains is 10 and 18, were easily prepared by reaction of the 4,4′-dicarboxy-2,2′-bipyridine with thionyl chloride and then with the appropriate n-alkylamine, in the presence of triethylamine, at reflux, under nitrogen atmosphere (Scheme 1). These ligands, obtained as white crystalline products after recrystallization from DMF/diethyl ether, have very scarce solubility in most of the common organic solvents; thus they were characterized by elemental analyses and IR spectroscopy, whose data are in the experimental section.

The reaction of $\mathbf{L^n}$ with AgOTf in a 1:2 metal-to-ligand stoichiometry (for 24 h under nitrogen atmosphere, in the dark) led to the formation of the ionic [$\mathbf{Ag(L^n)_2}$][**OTf**] complexes, **1-2**, (Scheme 2). These complexes, after recrystallization from chloroform/diethyl ether, were characterized by elemental analyses, IR and ^{1}H NMR spectroscopies.

In the cationic bis-chelated silver derivatives **1-2**, the silver atom, in a distorted tetrahedral geometry, is coordinated by the four N atoms of the two bipyridines, as already found in the crystal structure determination of non substituted 2,2′-bipyridine silver complexes with anions such as $(BF_4)^-$ and $(PF_6)^-$ [10,11]. The ionic nature of the triflate group is confirmed by the IR spectra which display a band at 1250 cm^{-1} [12,13].

The thermal behaviour of both ligands and complexes were investigated by polarized optical microscopy, differential scanning calorimetry (DSC), and temperature dependent powder X-ray diffraction (PXRD) measurements and the data are summarized in Tables 1 and 2.

As concerns the ligands, only $\mathbf{L^2}$, bearing the longest aliphatic chains, shows mesomorphism. In particular, after a crystal to crystal transition, $\mathbf{L^2}$ melts into the smectic C phase, as indicated by the typical schlieren texture and the powder diffraction pattern recorded at 176°C on cooling. The spectrum is characterized by three sharp reflections at low angles and one broad diffuse peak at high angle at the corresponding d spacing of 47.7, 23.6, 15.8 and 4.8 Å. The peaks

TABLE 2 X-ray Diffraction Data of Complexes **1-2**

Compound	Mesophase lattice constants/Å	d_{obs}/Å (d_{calcd}/Å)	Miller indices
$[(\mathbf{L^1})_2\mathbf{Ag}][\mathbf{OTf}]$ **1**	Col_r at 150°C	30.4 (30.4)	(1 1)
	$a = 55.5$	27.7 (27.7)	(2 0)
	$b = 36.3$	21.6 (22.1)	(2 1)
		19.4 (18.5)	(3 0)
		16.8 (16.5)	(3 1)
		15.0 (15.2)	(2 2)
		ca. 4.6	broad
$[(\mathbf{L^2})_2\mathbf{Ag}][\mathbf{OTf}]$ **2**	Col_hat 150°C	30.1 (30.1)	(1 0)
	$a = 34.9$	17.4 (17.4)	(1 1)
		15.2 (15.1)	(2 0)
		ca. 4.7	broad

at 23.6 and 15.8 Å are due to the second and third harmonic reflections. The diffuse nature of the broad peak in the wide angle region corresponds to short range correlation in the direction perpendicular to molecules within the layer plane. The lamellar mesophase is enantiotropically exhibited for several heating/cooling cycles.

Both four-chained $[\mathbf{Ag}(\mathbf{L^n})_2][\mathbf{OTf}]$ complexes **1** and **2,** show enantiotropic columnar mesomorphism, regardless the length of the substituents. The identification of the discotic phases was performed by observation of the typical optical textures: in particular a rectangular phase was attributed to complex **1** (Fig. 1a), while he fan-shaped texture with some linear defects and homeotropic domains (Fig. 1b) was observed for the hexagonal mesophase of **2**.

The reproducibility of the mesomorphism was checked with DSC on subsequent heating-cooling cycles only for $[(\mathbf{L^1})_2\mathbf{Ag}][\mathbf{OTf}]$ because

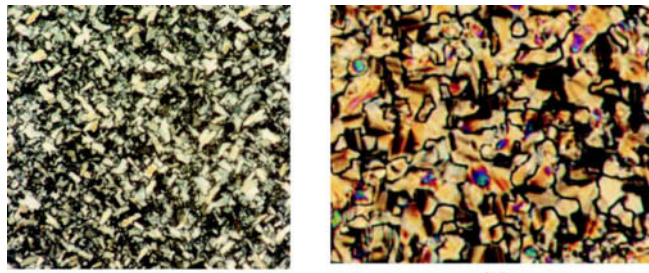


FIGURE 1 Optical texture: a) the Col_r texture of **1** at 150°C on cooling; (b) the Col_h phase of **2** at 200°C on heating.

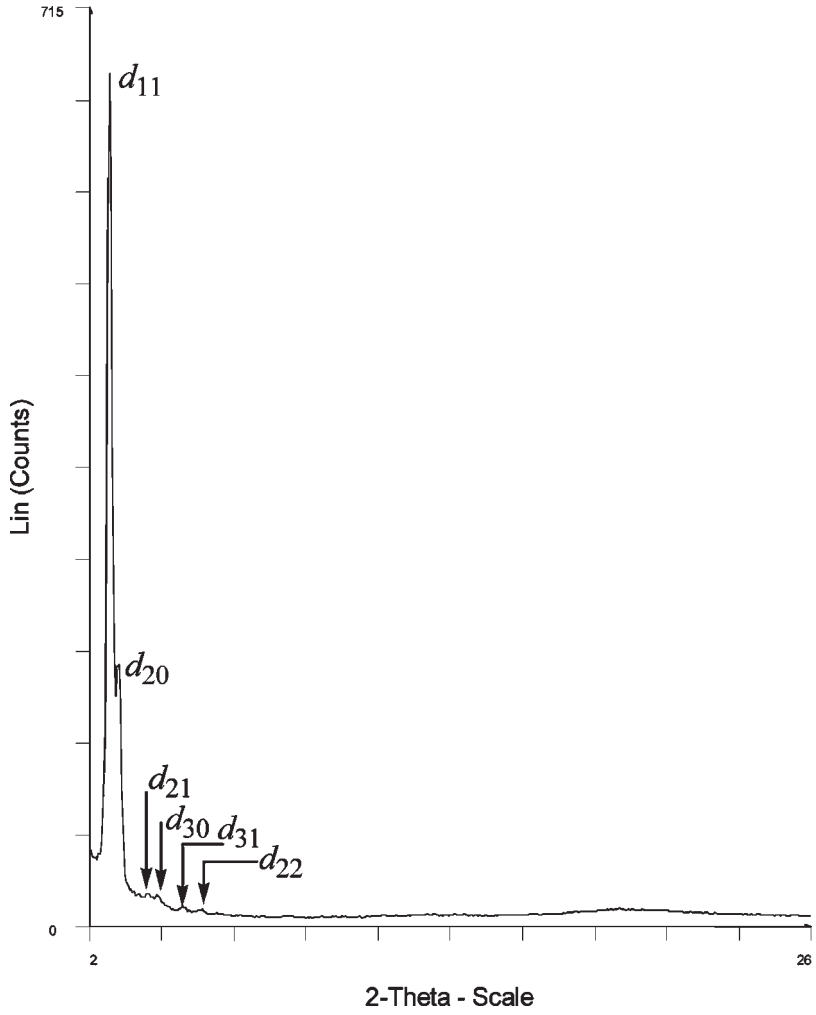


FIGURE 2 X-ray diffraction pattern of complex **1** at 150°C on heating.

an increase in the number of carbon atoms of the side chains was accompanied by decomposition on the clearing point for the $\mathbf{L^2}$ derivative, **2**.

The unequivocal identification of the symmetries of the phases was assigned after X-ray diffraction analysis. The XRD pattern of complex **1** shows a 2D rectangular lattice being characterized by two sharp fundamental peaks in the low angle region (Fig. 2). The less intense of these corresponds to the fundamental reflection (2 0), while

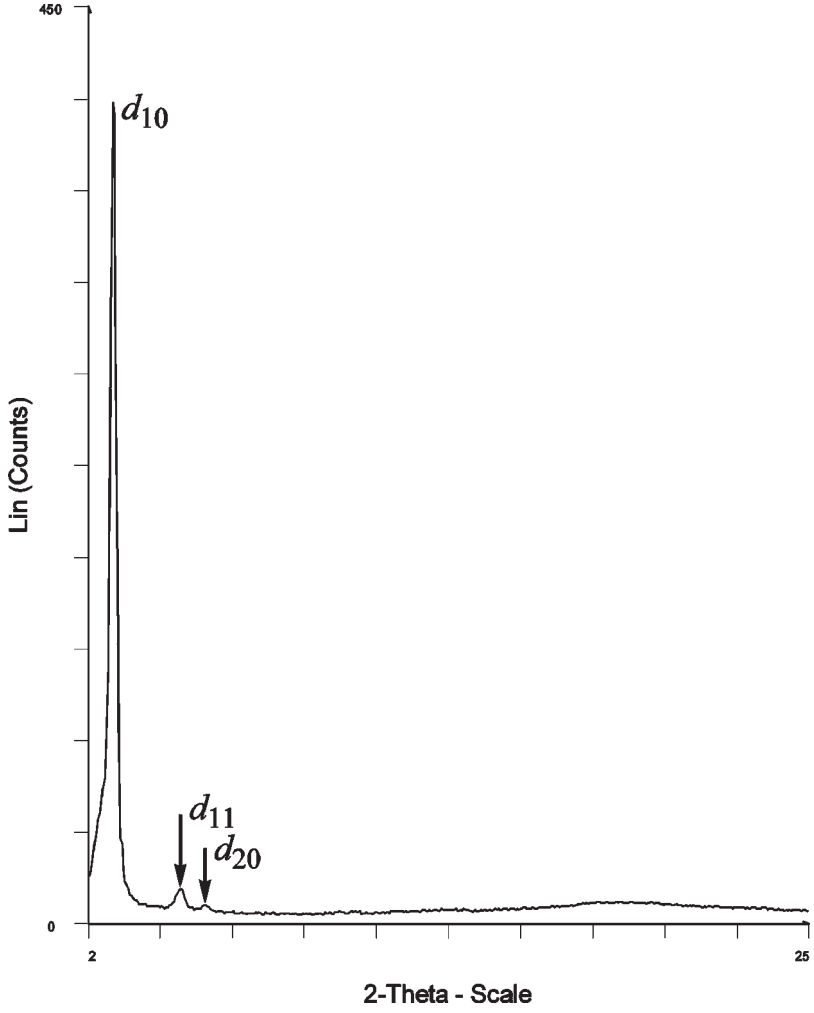


FIGURE 3 X-ray diffraction pattern of complex **2** at 150°C, on heating.

the more intense peak is associated with the two reflections (1 1) and (1–1) of equal intensity, with the (1 1) reflection being at the smaller angle, that is $d_{11} > d_{20}$ (Table 2). The presence of the (2 1) reflection implies a plane group *p*2*gg* for the mesophase, which is less common than the *c*2*mm* one and generally assigned for short chain length compounds [14]. This diffraction pattern corresponds to the rectangular constants a = 55.5 and b = 36.3 Å.

The mesophase changes from columnar rectangular to hexagonal arrangement with increasing the carbon number of the chains. In fact, the XRD pattern of complex **2** is typical of a two dimensional hexagonal lattice with the three peaks in the low angle region in the ratio $1:(3)^{1/2}:2$ (Fig. 3). The wide angle region displays a broad halo centred at 4.7 Å typical of liquid correlations between side chains (Table 2).

The mesophase crossover from rectangular to hexagonal phase has been observed in similar metallomesogenic systems and is generally attributed to the fact that shorter side chain complexes favor greater core interactions necessary for the formation of the Colr phases [15,16].

CONCLUSIONS

We have prepared and characterized new columnar four-chained metallomesogens build up through a metal-mediated self-assembly of non mesogenic or smectic 2,2′-bipyridine-4,4′-diamides. Both ionic bis-chelated silver(**I**) complexes [$(\mathbf{L^n})_\mathbf{2}\mathbf{Ag}$][**OTf**] show columnar mesomorphism. The length of the amidic substituents plays an important role on the mesomorphic and thermal behaviour of both ligands and complexes leading, for the ligands, to the promotion of the mesomorphism, and for the complexes to different symmetries of the columnar mesophases. However, the presence of the amidic functionality induces an ordered structural organisation, probably due to the ability to give rise to H-bonding interactions which lead to high transition temperatures.

Finally, by a careful choice of the molecular building blocks, it is possible to modulate the interactions responsible of the supramolecular architecture, and, starting from lamellar ligands, induce columnar mesomorphism in the corresponding complexes.

REFERENCES

[1] Kato, T. & Mizoshita, N. (2002). *Curr. Opin. Sol. State Mat. Sci.*, *6*, 579.
[2] Serrano, J. L. (1996). *Metallomesogens*, Weinheim: VCH.
[3] Donnio, B. & Bruce, D. W. (1999). Liquid Crystals II Metallomesogens. In: *Structure and Bonding*, Mingos, D. M. P. (Ed.), Springer, Vol. 95.
[4] Donnio, B., Guillon, D., Deschenaux, R., & Bruce, D. W. (2003). Metallomesogens. In: *Comprehensive Coordination Chemistry II*, McCleverty, J. A. & Meyer, T. J. (Eds.), Elsevier: Oxford, vol. 6.
[5] Date, R. W., Iglesias, E. F., Rowe, K. E., Elliot, J. M., & Bruce, D. W. (2003). *Dalton Trans.*, *10*, 1914–1931.
[6] Newkome, G. R., Patri, A. K., Holder, E., & Schubert, U. S. (2004). *Eur. J. Org. Chem.*, *22*, 235–254.

[7] Tschierske, C. (2000). *Angew. Chem. Int. Ed.*, *39*, 2454.
[8] Gharbia, M., Gharbi, A., Nguyen, H. T., & Malthête, J. (2002). *Curr. Opin. in Colloid and Interface Sci.*, *7*, 312.
[9] Pucci, D., Barberio, G., Crispini, A., & Ghedini, M. (2003). *Mol. Cryst. Liq. Cryst.*, *395*, 165.
[10] Constable, E. C., Housecroft, C. E., Neuburger, M., Poleschak, I., & Zehnder, M. (2003). *Polyhedron*, *22*, 93.
[11] Wu, H.-P., Janiak, C., Rheinwald, G., & Lang, H. (1999). *J. Chem. Soc., Dalton Trans.*, 183.
[12] Dixon, N. E., Jackson, W. G., Lancaster, M. J., Lawrance, G. A., & Sargeson, A. M. (1981). *Inorg. Chem.*, *20*, 470.
[13] Lawrance, G. A. (1986) *Chem. Rev.*, *86*, 17.
[14] Morale, F., Date, R. W., Guillon, D., Bruce, D. W., Finn, R. L., Wilson, C., Blake, A. J., Schröder, M., & Donnio, B. (2003). *Chem. Eur. J.*, *9*, 2484.
[15] Lai, C. K., Tsai, C.-H., & Pang, Y.-S. (1998). *J. Mater. Chem.*, *8*, 1355.
[16] Zheng, H. X., Lai, C. K., & Swager, T. M. (1995). *Chem. Mater.*, *7*, 2067.