

Tailoring “non conventional” ionic metallomesogens around an *ortho*-palladated fragment

Daniela Pucci *, Giovanna Barberio, Anna Bellusci, Alessandra Crispini, Mauro Ghedini

Centro di Eccellenza CEMIF.CAL-LASCAMM, Unità INSTM della Calabria, Dipartimento di Chimica, Università della Calabria,
Via P. Bucci Cubo 14/C, I-87030 Arcavacata (CS), Italy

Received 11 October 2005; received in revised form 16 November 2005; accepted 16 November 2005
Available online 20 December 2005

Abstract

A series of new ionic *ortho*-palladated mesogenic complexes $[\text{Pd}(\text{L})(4,4'\text{-R}^n\text{-bpy})][\text{X}]$ of unusual molecular shape have been prepared and characterised. The effect of slight structural changes on the molecular organization in the liquid crystalline phase is discussed in relation with their potential application as molecular materials.

© 2005 Elsevier B.V. All rights reserved.

Keywords: *Ortho*-palladation; Bipyridines; Phenylpyrimidines; Metallomesogens

1. Introduction

The actual interest in designing novel materials for high-tech applications is leading to drum up for liquid crystalline systems for which combination of the order and mobility helps their molecular organisation to change in reply to any external stimuli [1]. Thus, the investigation of new molecular motifs able to give rise to conventional liquid crystalline phases as well as to unusual mesophase morphologies, has become one of the most exciting areas of chemical research. The common design principle based on the shape and the symmetry of the archetypal mesogenic molecules is giving way to new guiding for the formation of complex superstructures and mesophase morphologies [2] based both on new molecular shapes (i.e. banana-shaped [3], hollow-cone [4], polycatenar [5], dendritic [6], λ -shaped [7] and inverted discotic [8] molecules) and on micro-segregation between incompatible units within the molecules [2b].

In this context metal coordination of organic ligands provides a new concept for the synthesis of “non conventional” systems whose molecular architecture can be controlled by

the modulation of different and tunable synthons: the metal–ligand fragment as central unit, the number of flexible chains at the periphery, the type of complementary ligands completing the coordination sphere of the metal ion, the counter-ion when the complex is ionic [9]. In particular the cyclopalladation proved to be a good synthetic strategy to obtain new functional liquid crystals exhibiting a variety of new properties strongly affected by little changes of single tectons and global molecular shape, such as, for example, *ortho*-metallated mesogens based on the combination of rod-like phenylpyrimidines with bent or half-disk-shaped diketonates, for which structural changes led to discontinues transitions from a lamellar to columnar organization in the mesophase [10].

Recently a new way for tailoring mesomorphic properties is based on the first example of cyclometallated ionic mesogen, **I** in Chart 1, which was the leader of a new thermotropic class of metallomesogens [11]. Changes in the *N,N* chelating ligands and in the type of counter-ions caused significant variations in the liquid crystalline properties of these species, preventing in some cases the existence of any mesomorphism. A further example of ionic *ortho*-palladated complex has been successively reported, containing the 8-methylquinoline as cyclopalladated ligand and a bipyridine substituted in 3,3'-position with dodecyloxy

* Corresponding author. Tel.: +39 09 84 49 20 64; fax: +39 09 84 49 20 66.

E-mail address: d.pucci@unical.it (D. Pucci).

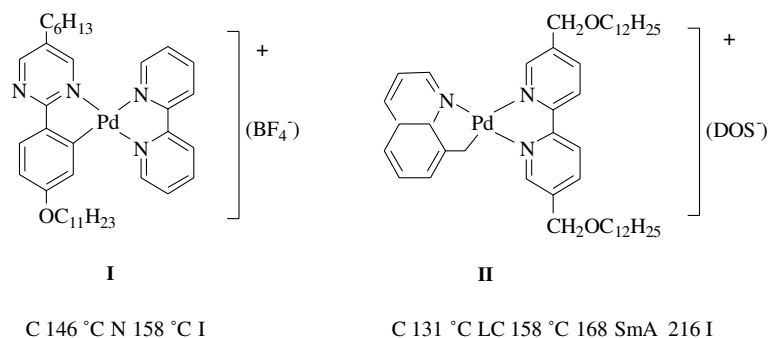


Chart 1.

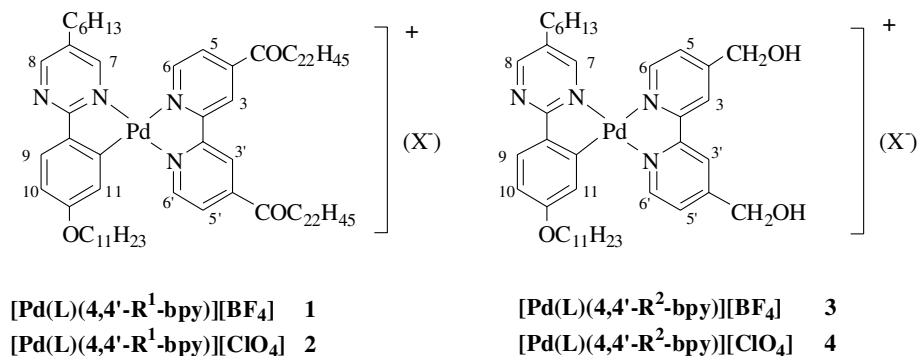


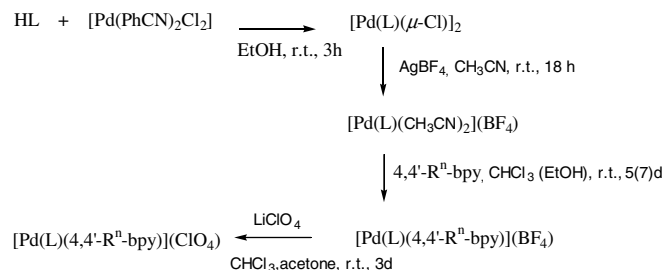
Chart 2.

chains as complementary ligand, **II** in Chart 1. The unusual molecular shape of this complex, intermediate between a rod and a disc like, induced a mixed mesomorphism consisting in a lamellar phases and a lamello-columnar phase [12].

The recent availability of a method for the syntheses of 2,2'-bipyridines disubstituted in 4,4'-positions [9b,9c] has prompted us to investigate the liquid crystalline behaviour of a new class of *ortho*-palladated complexes whose molecular shape can be considered at the cross-over point between calamitics and discotics. Herein we report the synthesis and the full characterization of a series of cationic *ortho*-palladated complexes of general formula $[\text{Pd}(\text{L})(4,4'\text{-R}^n\text{-bpy})][\text{X}]$ (Chart 2) by the combination of a nematic rod-like phenylpyrimidine (**L**) with laterally substituted non mesogenic bipyridines, (4,4'-Rⁿ-bpy).

2. Results and discussion

The synthetic pathway used to obtain these compounds is illustrated in Scheme 1. The dinuclear cyclopalladated complex $[\text{Pd}(\text{L})(\mu\text{-Cl})_2]$ [13] obtained by *ortho*-palladation of the 5-(1-hexyl)-2-[4'-(1-undecyloxy)phenyl]pyrimidine ligand **L** with an equimolar amount of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$, was used as precursor in the bridge splitting reaction with the neutral chelating (4,4'-Rⁿ-bpy) ligands [9b,9c] was performed in a two step process. All complexes have been fully characterized by ¹H NMR, FT-IR and elemental analysis that confirm the stoichiometry of the complexes.

Scheme 1. Synthetic route to $[\text{Pd}(\text{L})(4,4'\text{-R}^n\text{-bpy})](\text{X})$ complexes.

The presence, in the IR spectra of a band at 1086 cm^{-1} and at 1122 cm^{-1} , corresponding to the absorption of a tetrafluoroborate and of a perchlorate group, respectively, supports the ionic nature of all complexes.

The thermal behaviour of complexes **1–4** was investigated by optical microscopy (crossed polarizer), differential scanning calorimetry and temperature dependent powder X-ray diffraction measurements and the thermal data are summarized in Table 1. With respect to complex **I** the unusual molecular shape induced by the introduction of lateral chains in 4,4'-positions of the bipyridine ligand, significantly influences the mesophase type. Indeed while **I** exhibited only the more disordered calamitic mesophase, that is the Nematic one, a lamellar mesomorphism is found for the entire series $[\text{Pd}(\text{L})(4,4'\text{-R}^n\text{-bpy})][\text{X}]$.

The identification of the mesophases was firstly performed by observation of the optical textures, namely a fine

Table 1
Optical and thermal data of complexes

Complex ^a	Transition ^a	<i>T</i> (°C) ^a	ΔH (kJ mol ⁻¹) ^c	<i>d</i> (Å) ^b
1	Cr–Cr'	50.1	34.2	41.6
	Cr'–SmC ₂	82.9	10.7	
	SmC ₂ –I	146.1	18.6	
2	Cr–SmC ₂	49.8	4.1	42.3
	SmC ₂ –I	148.9	19.9	
3	Cr–SmAd	204.6	16.4	50.0
	SmAd–Idec.	234.6		
4	Cr–SmAd	210.3	28.5	51.5
	SmAd–Idec.	212.3		

^a Cr, Crystal; SmA, Smectic A; I, Isotropic liquid; dec, decomposition.

^b Layer spacing *d* (Å), derived from diffraction patterns.

^c Values obtained on heating at the first cycle, at a rate of 10 °C/min.

schlieren texture, consistent with a Smectic C (SmC) phase, for complexes **1** and **2**, or the typical fan like texture of the Smectic A (SmA) phase, for complexes **3** and **4**.

By studying these complexes with X-ray diffraction (XRD) we were able to better understand the nature of the mesophases. In particular, the XRD patterns of complexes **1** and **2** (4,4'-R¹-bpy) exhibited sharp inner reflections and diffuse halos, consistent with a layered structure. The reflections at low angle consist of a set of *00n* peaks, where *n* is an integer (*n* = 1–3) and *d* of 41.6 and 42.3 Å is the layer spacing for **1** and **2**, respectively (Fig. 1(a)). The diffuse outer halo centered at 4.6–4.7 Å is associated with the short range liquid-like positional ordering of the hydrocarbon chains.

In both cases the values of the layer thickness *d* are nearly 1.4 times the molecular length *L* (~30 Å), as calculated taking into account the phenylpyrimidine ligand with

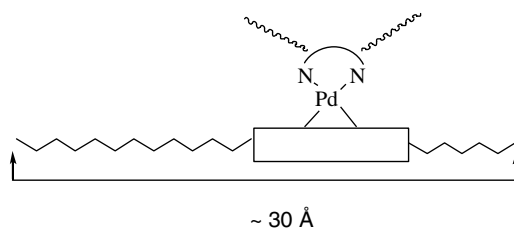


Fig. 2. Schematic representation of the molecular length in complexes **1–4**.

the alkyl and alkoxy chains in their *trans* extended conformation (Fig. 2) and already reported for similar phenylpyrimidine complexes [14]. This finding is indicative of the presence of either a partially bilayered SmA_d phase or the direct analogous tilted bilayered SmC₂ [15,16]. However, the existence of a schlieren texture in **1** and **2** is incompatible with the presence of a SmA mesophase, allow us to conclude that the structure of the mesophase in these complexes is the SmC₂ phase.

A remarkable variation in the layer spacings of the lamellar mesophase and in the thermal properties is produced when a strongly polar group such a short CH₂OH is present in (4,4'-R²-bpy) derivatives. The XRD spectra of complexes **3** and **4** confirmed the presence of a SmA phase in accordance with the optical textures and the actual values of the layer thickness (Table 1) are consistent with a partially bilayer SmA_d mesophase (Fig. 1(b)). Therefore, the effect of introducing groups on the bipyridine moiety, able to form strong intermolecular interactions, causes a distinct increase of both the clearing temperatures and the layer spacing within the mesophase when compared to complexes **1** and **2**. For both compounds the transition from liquid crystal to I phase is accompanied by decomposition.

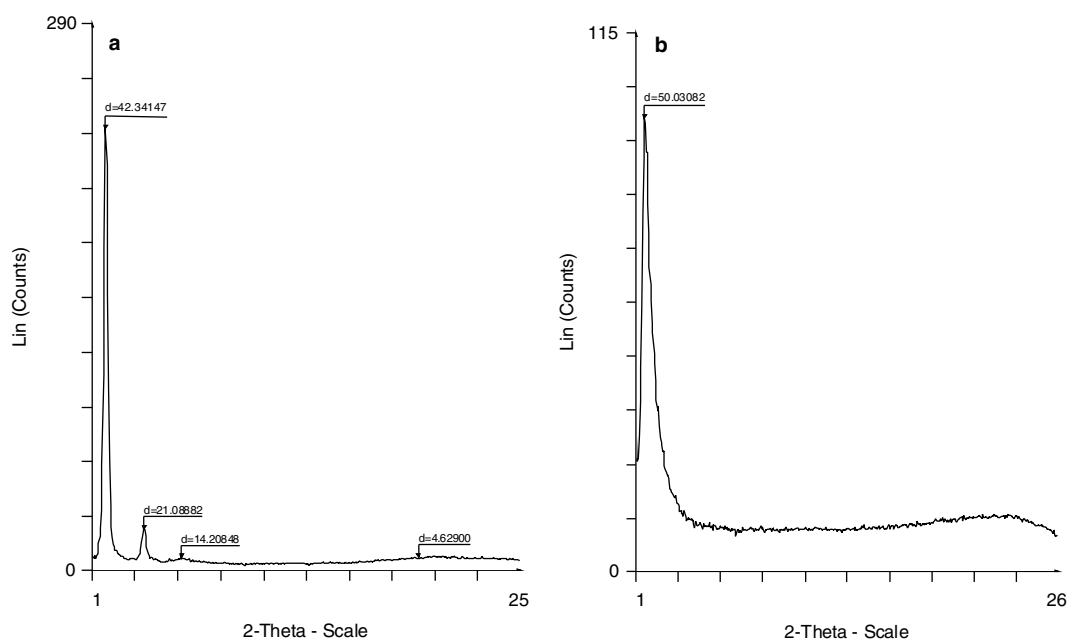


Fig. 1. XRD patterns of **2** recorded at 70 °C on heating (a) and **3** recorded at 220 °C on heating (b).

Comparison of the mesogenic behaviour of this class of complexes with the unsubstituted **1** shows that the effect of the presence and the position of substituents on the bipyridine fragment is a key factor to control the mesomorphism in these systems. The presence of the strong hydrophobic interactions of the alkyl chains in complexes **1** and **2**, and hydrogen bonds in complexes **3** and **4**, increases the order within the mesophase promoting a transition from nematic to lamellar organization.

3. Conclusions

Four new ionic palladium complexes of general formula $[\text{Pd}(\text{L})(4,4'\text{-R}''\text{-bpy})][\text{X}]$, containing as *ortho*-palladated fragment, the 5-(1-hexyl)-2-[[4'-(1-undecyloxy)phenyl]]pyrimidine ligand and a 4,4'-disubstituted-2,2'-bipyridine (bpy) as bidentate chelating ligand, have been synthesised. The thermal and mesomorphic trend observed for these complexes confirms that the molecular design of cyclopalladated mesogens can produce, more than purely organic species, molecular shapes easily modulated. Indeed, they have been shown to be very versatile systems for which changes of only one tecton (the bpy fragment, for example) led to noticeable modifications on the molecular organization in the liquid crystalline phase [9a]. However, no significant difference in the mesomorphic properties is observed by changing the anion from BF_4^- to ClO_4^- , which, in this case, is consistent with the small variation in the size and the nature of these counterions.

This flexibility in the design is a very distinctive feature which could have high potentiality to reach easily selected mesomorphic properties suitable for new applications. For example, technologically relevant photorefractive materials are particularly attractive when based on liquid crystals, especially smectics, for their high spontaneous birefringence and for their field-induced refractive index control mechanism [17]. Recently, we have reported on the photorefractive properties of chiral smectic C phases formed by cyclopalladated complexes in which, for the first time, photorefractivity is an intrinsic property, not induced by the addition of photosensitive dopants [18]. Therefore we are persuaded to continue the investigation on the influence of the molecular topology on the mesogenic properties, for example with the introduction of chiral groups on the bipyridine moieties of the herein described systems.

4. Experimental

Commercially available starting ligand, 5-(1-hexyl)-2-[[4'-(1-undecyloxy)phenyl]]pyrimidine, [HL] (Merk E.) and standard chemicals were used as supplied. Infrared spectra were recorded on a Spectrum One FT-IR Perkin–Elmer spectrometer and ^1H NMR spectra at 300 K on a Bruker AVANCE-300 spectrometer working at 7.04 T, in CDCl_3 solution, with TMS as internal standard. Elemental analyses were performed 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 Pyris 1 Differential Scanning Calorimeter with a heating and cooling rate of $10\text{ }^\circ\text{C}/\text{min}$. 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 $\text{Cu K}\alpha$ radiation; the high sensitive area detector was placed at a distance from the sample of 10 cm and equipped with a CalCTec (Italy) heating stage. The samples were heated at a rate of $5.0\text{ }^\circ\text{C min}^{-1}$ to the appropriate temperature. Measurements were performed by charging samples in Lindemann capillary tubes with inner diameter of 0.07 mm.

4.1. Synthesis of complexes **1** and **3**

To a solution of AgBF_4 (35.3 mg, 0.180 mmol) in acetonitrile (5 mL) was added the complex $[\text{Pd}(\text{L})(\mu\text{-Cl})_2]$ (100 mg, 0.090 mmol); the mixture was stirred for 18 h with the vessel protected from the light and filtered to remove AgCl . The filtrate was evaporated to dryness to give the residue solvate intermediate $[\text{Pd}(\text{L})(\text{MeCN})_2][\text{BF}_4]$.

1 was obtained by treating the solvate species with an equimolar amount of [4,4'- R^1 -bpy] (155 mg, 0.180 mmol) dissolved in chloroform (10 mL). The resulting orange solution was stirred at r.t. for 5 days. After concentration and addition of ethanol, the product was obtained by filtration (256 mg, 97%). ^1H NMR (300 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, TMS): δ 2.90 (t, $^3J = 7.7\text{ Hz}$, 2H, CH_2), 3.97 (t, $^3J = 6.2\text{ Hz}$, 2H, OCH_2), 4.47 (m, 4H, COOCH_2), 6.54 (s, 1H, H-11), 6.77 (d, $^3J = 8.6\text{ Hz}$, 1H, H-10), 7.76 (d, $^3J = 8.6\text{ Hz}$, 1H, H-9), 8.40 (m, 2H, H-5,5'), 8.73 (m, 4H, H-6,6',7,8), 9.21 (d, $^4J = 1.4\text{ Hz}$, 2H, H-3,3'). IR (KBr): $\nu = 1728$ (C=O), 1084 (BF_4) cm^{-1} . Anal. Calc. for $\text{C}_{83}\text{H}_{137}\text{BF}_4\text{N}_4\text{O}_5\text{Pd}$ (1464.25): C, 68.08; H, 9.43; N, 3.83. Found: C, 68.01; H, 9.54; N, 3.79%.

3 was obtained by treating the solvate species with [4,4'- R^2 -bpy] (39 mg, 0.180 mmol) dissolved in ethanol (10 mL). The mixture was stirred at r.t. for 7 days. The product was obtained (88 mg, 60%) after filtration and recrystallization from ethanol. ^1H NMR (300 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, TMS): δ 2.52 (t, $^3J = 7.4\text{ Hz}$, 2H, CH_2), 3.82 (t, $^3J = 6.4\text{ Hz}$, 2H, OCH_2), 4.64 (s, 4H, CH_2OH), 6.41 (s, 1H, H-11), 6.53 (d, $^3J = 8.5\text{ Hz}$, 1H, H-10), 7.44 (d, $^3J = 8.5\text{ Hz}$, 1H, H-9), 7.58 (m, 2H, H-5,5'), 8.25 (m, 3H, H-6,6',8), 8.46 (s, 1H, H-7), 8.54 (s br, 2H, H-3,3'). IR (KBr): $\nu = 1619$ (CH_2OH), 1086 (BF_4) cm^{-1} . Anal. Calc. for $\text{C}_{39}\text{H}_{53}\text{BF}_4\text{N}_4\text{O}_3\text{Pd}$ (819.10): C, 57.19; H, 6.52; N, 6.84. Found: C, 56.98; H, 6.84; N, 6.51%.

4.2. Synthesis of complexes **2** and **4**

The perchlorate derivatives **2** and **4** have been obtained by metathetical reaction of **1** (80 mg, 0.055 mmol) and **3** (123 mg, 0.150 mmol), dissolved in chloroform, with an

excess (1:5) of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, in acetone. The resulting solution was stirred at r.t. for 3 days. The filtrate was evaporated to dryness and the residue was recrystallised by water/ethanol.

2 (33 mg, 41%). ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ 2.90 (t, $^3J = 7.6$ Hz, 2H, CH_2), 3.96 (t, $^3J = 6.2$ Hz, 2H, OCH_2), 4.50 (t, $^3J = 6.7$ Hz, 4H, COOCH_2), 6.53 (s, 1H, H-11), 6.75 (d, $^3J = 8.5$ Hz, 1H, H-10), 7.73 (d, $^3J = 8.5$ Hz, 1H, H-9), 8.37 (d, $^3J = 5.0$ Hz, 2H, H-5,5'), 8.65 (s, 1H, H-8), 8.70 (s, 1H, H-7), 8.75 (d, $^4J = 1.2$ Hz, 2H, H-3,3'), 9.20 (d, $^3J = 5.0$ Hz, 2H, H-6,6'). IR (KBr): $\nu = 1727$ ($\text{C}=\text{O}$), 1121 (ClO_4) cm^{-1} . Anal. Calc. for $\text{C}_{83}\text{H}_{137}\text{ClN}_4\text{O}_9\text{Pd}$ (1476.90): C, 67.50; H, 9.35; N, 3.79. Found: C, 67.19; H, 9.52; N, 3.78%.

4 (94 mg, 75%). ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ 2.51 (t, $^3J = 7.4$ Hz, 2H, CH_2), 3.79 (t, $^3J = 6.4$ Hz, 2H, OCH_2), 4.93 (s, 4H, CH_2OH), 6.36 (s, 1H, H-11), 6.48 (d, $^3J = 8.5$ Hz, 1H, H-10), 7.39 (d, $^3J = 8.5$ Hz, 1H, H-9), 7.59 (s br, 2H, H-5,5'), 8.20 (s, 3H, H-3,3',8), 8.42 (s, 1H, H-7), 8.51 (s br, 2H, H-6,6'). IR (KBr): $\nu = 1621$ (CH_2OH), 1122 (ClO_4) cm^{-1} . Anal. Calcd for $\text{C}_{39}\text{H}_{53}\text{ClN}_4\text{O}_7\text{Pd}$ (831.75): C, 56.32; H, 6.42; N, 6.74. Found: C, 55.99; H, 6.37; N, 6.72%.

Acknowledgements

This work was partly supported by the Italian Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) through the INSTM-FIRB and Centro di Eccellenza CE-MIF.CAL Grants.

References

- [1] M. O'Neill, S.M. Kelly, *Adv. Mater.* 15 (2003) 1135.
- [2] (a) B. Chen, X.B. Zeng, U. Baumeister, S. Diele, G. Ungar, C. Tschierske, *Angew. Chem. Int. Ed.* 43 (2004) 4621; (b) C. Tschierske, *J. Mater. Chem.* 11 (2001) 647.
- [3] (a) T.C. Lubenski, *Science* 288 (2000) 2146; (b) N. Gimeno, B. Ros, J.L. Serrano, M.R. de la Fuente, *Angew. Chem. Int. Ed.* 43 (2004) 5235.
- [4] C. Tschierske, *Nature* 419 (2002) 681, News and Views.
- [5] (a) H.-T. Nguyen, C. Destrade, J. Malthete, *Adv. Mater.* 9 (1997) 375; (b) B. Donnio, B. Heinrich, H. Allouchi, J. Kain, S. Diele, D. Guillon, D.W. Bruce, *J. Am. Chem. Soc.* 126 (2004) 15258.
- [6] (a) A.G. Cook, U. Baumeister, C. Tschierske, *J. Mater. Chem.* 15 (2005) 1708; (b) L. Gehringer, C. Bourgoigne, D. Guillon, B. Donnio, *J. Am. Chem. Soc.* 126 (2004) 3856.
- [7] A. Yamaguchi, I. Nishiyama, J. Yamamoto, H. Yokoyama, A. Yoshizawa, *J. Mater. Chem.* 15 (2005) 280.
- [8] S. Höger, X.H. Cheng, A. Ramminger, V. Enkelmann, A. Rapp, M. Mondeshki, I. Schnell, *Angew. Chem. Int. Ed.* 44 (2005) 2801.
- [9] (a) R.W. Date, E.F. Iglesias, K.E. Rowe, J.M. Elliott, D.W. Bruce, *Dalton Trans.* (2003) 1914; (b) D. Pucci, G. Barberio, A. Bellusci, A. Crispini, M. La Deda, M. Ghedini, E.I. Szerb, *Eur. J. Inorg. Chem.* (2005) 2457; (c) G. Barberio, A. Bellusci, A. Crispini, M. Ghedini, A. Golemme, P. Prus, D. Pucci, *Eur. J. Inorg. Chem.* (2005) 181.
- [10] (a) J. Dupont, C.S. Consorti, J. Spencer, *Chem. Rev.* 105 (6) (2005) 2527; (b) T. Hegmann, J. Kain, S. Diele, B. Schubert, H. Bogel, C. Tschierske, *J. Mater. Chem.* 13 (2003) 991.
- [11] M. Ghedini, D. Pucci, *J. Organomet. Chem.* 395 (1990) 105.
- [12] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem. Int. Ed.* 37 (1998) 1255.
- [13] M. Ghedini, D. Pucci, G. De Munno, D. Viterbo, F. Neve, S. Armentano, *Chem. Mater.* 3 (1991) 65.
- [14] M. Ghedini, D. Pucci, R. Bartolino, O. Francescangeli, *Liq. Cryst.* 13 (1993) 255.
- [15] D. Demus, J. Goodby, G.W. Gray, H.W. Spiess, V. Vill (Eds.), *Handbook of Liquid Crystals*, Wiley-VCH, 1998.
- [16] O. Francescangeli, D. Rinaldi, M. Laus, G. Galli, B. Gallot, *J. Phys. II France* 6 (1996) 77.
- [17] (a) G.P. Wiederrecht, B.A. Yoon, M.R. Wasielewski, *Adv. Mater.* 12 (2000) 1533; (b) T. Sasaki, Y. Kino, M. Shibata, N. Mizusaki, A. Katsuragi, Y. Ishikawa, T. Yoshimi, *Appl. Phys. Lett.* 78 (2001) 4112.
- [18] (a) M. Talarico, G. Barberio, D. Pucci, M. Ghedini, A. Golemme, *Adv. Mater.* 15 (2003) 1374; (b) M. Talarico, R. Termine, G. Barberio, D. Pucci, M. Ghedini, A. Golemme, *Appl. Phys. Lett.* 84 (2004) 1034.