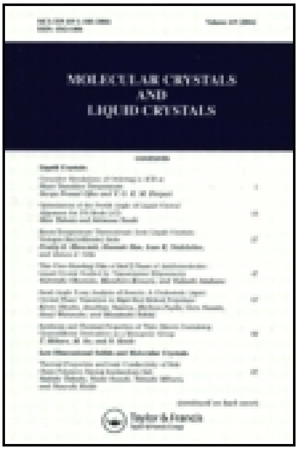

Molecular Crystals and Liquid Crystals

New Double-Decker Phthalocyanine Metallomesogens

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New Double-Decker Phthalocyanine Metallomesogens

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The valence state and the mesomorphic behaviors of a homologous series of new cerium phthalocyanine double-decker complexes bearing thioalkyl substituents are described. Spectroscopic studies and Single crystal X-Ray crystallography data revealed that the metal center in this lanthanide double-decker complex is tetravalent making the whole molecule neutral and the two ligands structurally equivalent. As a consequence, the thermal stability of their mesophase is enhanced compared to those of other lanthanide phthalocyanine complexes. Moreover, these compounds show a strong tendency towards homeotropic alignment of their hexagonal columnar (*Col*$_h$) *mesophase on a glass substrate, which persist at room temperature (glass transition).*

Keywords: cerium phthalocyanine; Discotic liquid crystals; double-decker complexes; homeotropic alignment

INTRODUCTION

Phthalocyanine (Pc) is a polyconjugated aromatic system much studied over the last two decades in the search for new electronic materials [1]. The columnar arrangement of these molecules in the mesophase indeed make them attractive candidate for the preparation of conductive materials with one-dimensional conduction pathway [2]. One of the best reported semiconducting material so far is the lutetium double-decker complex **(1)** (Scheme 1, left)

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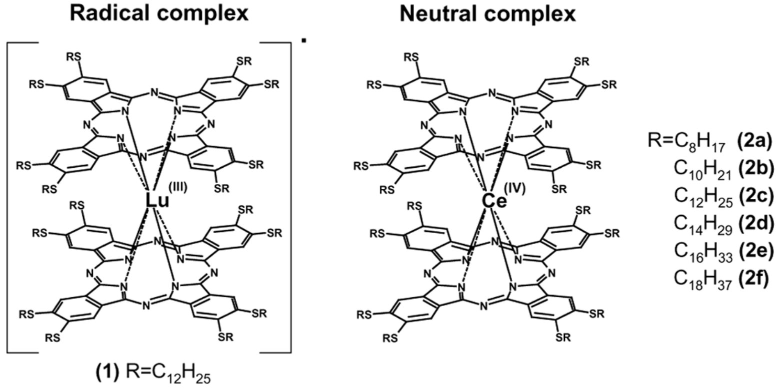

SCHEME 1 Lutetium and cerium phthalocyanine double-decker complexes.

where the central lanthanide ion is sandwiched between 2 phthalocyanine ligands [3].

In this complex, one of the Pc ligand is dianionic whereas the other is radical. As a consequence, the structure of this latter is more distorted [4]. However on heating, both rings become structurally equivalent due to delocalization of the free electron onto both Pc rings [5]. Carrier mobilities as fast as $0.7\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ have been recorded in their mesophases by pulse-radiolysis time resolved microwave conductivity technique [3]. Unfortunately, no spontaneous or controllable alignment of the molecules on a substrate, which is an important factor for device fabrication, could be achieved with compound **(1)**.

Compared to other lanthanide phthalocyanine mesogens [3,5], rather few substituted cerium phthalocyanine complexes have been reported [6]. Interestingly, the cerium atom in those complexes was found to adopt an intermediate valence comprised between 3 and 4, thus making the whole complex either neutral or radical, depending on the type of tetrapyrrole ring attached to the central metal ion [6].

In this work, a homologous series of new thioalkylated double-decker cerium phthalocyanine complexes **(2a)**–**(2f)** (Scheme 1, right), were synthesised and their mesomorphism were clarified by DSC, polarized optical microscopy and X-Ray diffraction for the tendency of spontaneous alignment on substrate.

EXPERIMENTAL

Compounds **(2a)**–**(2f)** were prepared by a modification of the method described by Ng *et al.* [7]. In our procedure, a slight excess (~0.5) of anhydrous cerium trichloride was used to avoid formation of the metal-free phthalocyanine derivative. The products were satisfyingly characterised by ^{1}H NMR, MALDI, IR, UV-Vis. spectroscopy as well as elemental analysis (C, H, and N).

The phase transition temperature and enthalpy changes were measured by differential scanning Calorimetry (DSC, TA instrument DSC2920) and the microscopic observation of the optical textures (Olympus BH2 and Mettler FP90 hot stage). The mesophase were identified by X-Ray diffraction at temperatures corresponding to the mesophase and the glass or crystal phase using a Rigaku RINT 2500 HF equipped with a hand-made hot stage. Temperature dependence electronic spectra and UV-visible spectra were measured on a spectrophotometer Shimadzu UV2500PC UV-Vis as a cast film or in solution in CH_2Cl_2. Single X-Ray measurements were performed by Dr M. Shiro (Rigaku). Near-IR spectra were obtained on a HITACHI U-4100 UV/Vis/NIR spectrophotometer.

RESULTS AND DISCUSSION

The weak absorption band at 494 nm on the UV-Vis. spectrum of **(2f)** (Fig. 1, left) as well as the absence of absorptions characteristic of phthalocyanine radical anion complexes in the region 800–900 and 1400–1700 nm on the near-IR spectrum of **(2f)** (Fig. 1, right) suggest that the Pc ligands are dianionic. Therefore, the cerium atom in this sandwich compound has principally an oxidation state IV. This also explains the possibility of obtaining well-defined ^{1}H NMR spectra for the whole series of compounds **(2a)–(2f)**. The partial delocalization of the single electron in the 4f orbital of the cerium ion onto the π-orbital of the ligands is thought to responsible for the neutrality of these cerium complexes [8].

The crystal structure of the short chain homologue **(2a)** presents some similarity with the previously reported lanthanide phthalocyanine complexes [4]. The cerium is eightfold coordinated by the isoindole nitrogens of the two phthalocyanine rings. The average calculated staggering angle formed between the two Pc rings is 43° with those two being almost parallel to each other. The distance between them is about 3.23 Å. The Pc ligands are distorted from planarity (4.2–8.7°) and are, therefore, concave but structurally equivalent. Moreover in their crystal packing, the molecules adopt a slip columnar arrangement.

All compounds show birefringence on heating which clear into an isotropic liquid at higher temperature. Their mesophase temperature ranges and enthalpy changes are shown in Table 1. Some trace of decomposition before reaching the clearing temperature could be seen

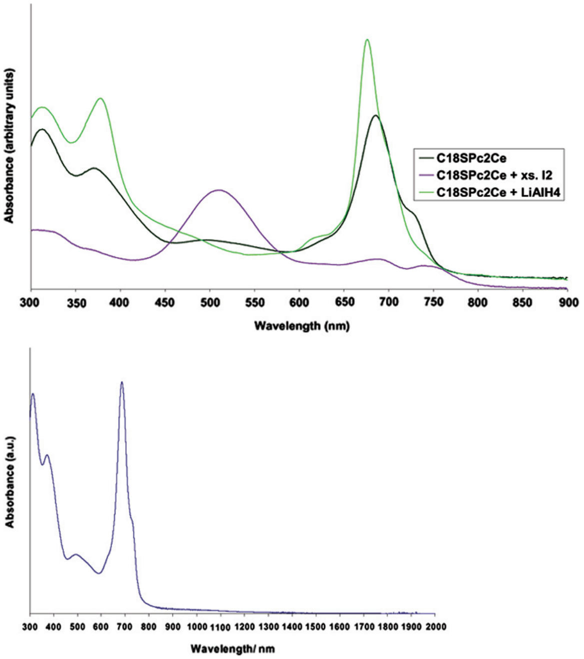

FIGURE 1 UV-Vis. spectra (left) of **(2f)** (dark green) in $CHCl_3$, its oxidized (purple) and reduced derivatives (green). Near-IR spectrum of **(2f)** in $CHCl_3$ (right).

for the C_8 homologue **(2a)**. The DSC thermograms of C_{10}–C_{14} homologues (**2b**)–(**2d**) show three reproducible transitions whereas only two are seen for the longer chain homologues (**2e**) and (**2f**). The mesophase temperature range of this series is wider than those of other lanthanide double-decker compounds having the same ligands [3].

TABLE 1 Mesophase Temperature Ranges and Enthalpy Changes of Compounds (**2a**)–(**2f**)

		T/°C (Enthalpy/kJ mol^{-1})			
Homologue	n	Cr => Col_{hd}	Cr => Col_{ho}	Col_{ho} => Col_{hd}	Col_{hd} => Iso
(2a)	8	95 (138)			257 (17)
(2b)	10		4 (22)	56 (8)	217 (11)
(2c)	12		– 3 (59)	47 (3)	180 (11)
(2d)	14		31 (104)	47 (4)	156 (13)
(2e)	16	49 (118)			139 (13)
(2f)	18	53 (364)			119 (12)

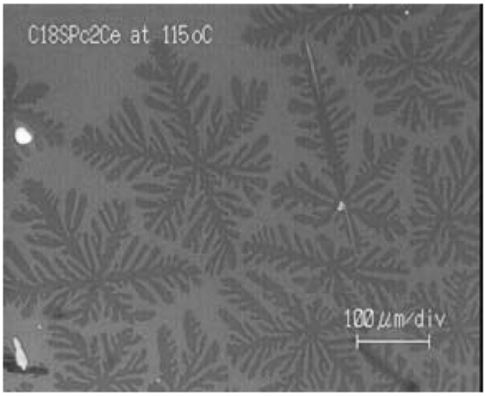

FIGURE 2 Dendritic growth view under uncrossed polarized light.

A fan texture characteristic of a columnar hexagonal mesophase (Col_h) was seen on the polarized microscope for all compounds before clearing as an isotropic liquid. This fan texture gradually changed to a mosaic like texture at lower temperature for the homologues (**2b**)–(**2d**). On the slower cooling (2°C/min) hexagonal dendritic growths along with some weak disclinations could be seen under uncrossed polarised light (Fig. 2). This phenomenon has been already observed with other phthalocyanine mesogens [9]. It corresponds to large area where the molecules spontaneously homeotropically align to the substrate. This behaviour makes these compounds good candidates for the measurement of their charge carrier mobility by TOF technique. Interestingly, microscopic observation also revealed that the homeotropic columnar alignment of these compounds could persist down to room temperature (glass transition) without any sign of crystallisation observed.

Powder X-ray diffraction analyses were performed in order to assign the type of mesophases described herein. The high temperature mesophase observed for all compounds was assigned as hexagonal disordered columnar, (Col_{hd}) one, considering that the reflections in the small angle region show a spacing ratios of $1{:}1/\sqrt{3} : 1/2 : 1/\sqrt{7} : 1/3 : 1/4$ and no reflections due to the stacking distances in the wide angle region could be seen (Fig. 3, left).

However, this latter could be detected on the X-ray diffraction pattern (Fig. 3, right) of the low temperature mesophase of (**2b**)–(**2d**). As a result, this mesophase was assigned as hexagonal ordered columnar, Col_{ho}. The broad halo also present in the wide angle region at

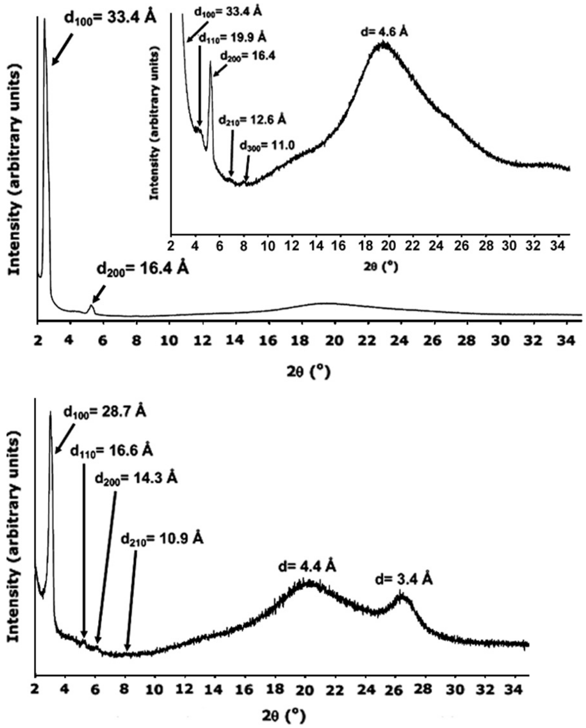

FIGURE 3 X-Ray diffraction pattern of (**2f**) at 80°C (left) and (**2c**) at 22°C (right).

ca. 4.4 Å (Fig. 3, right) confirms that these compounds are mesogenic at room temperature.

The reflections characteristic of a hexagonal columnar arrangement of the molecules were still present on the X-Ray patterns of (**2e**)–(**2f**) at room temperature thus confirming that these compounds are in glassy states at this temperature. However, the sharp reflection in the wide angle region at *ca.* 4.2 Å indicates that the thioalkyl chains are partially crystallized within the hexagonal packing of the central phthalocyanine cores.

The absence of splitting for the Q band on the temperature-dependent electronic spectra of a cast film of (**2f**) at as a glassy solid at 25°C, in its mesophase at 80°C or as an isotropic liquid at 130°C also confirms that the molecules keep a similar cofacial or slipped arrangement at these temperatures.

CONCLUSION

A homologous series ofs new double-decker cerium phthalocyanine mesogens was successfully prepared. In these complexes, the cerium atom is tetravalent with both ligands being concave. As a result, the thermal stability of their mesophase is enhanced compared to those of other double-decker phthalocyanine mesogens [3]. All homologues exhibited $\mathrm{Col_{hd}}$ mesophases prior to melting to the isotropic liquid. Long range orders within the hexagonal columnar mesophases were observed for all homologues at lower temperature ($\mathrm{Col_{ho}}$). XRD studies showed that the long chain homologue C_{16} (**2e**) & C_{18} (**2f**) are in fact in glassy states at room temperature whereas shorter chain homologues C_{10}–C_{14} (**2b**)–(**2d**) are liquid crystals. Interestingly, these compounds have strong tendency for spontaneous homeotropic alignment on non-treated glass substrates.

All these properties make these compounds promising materials for photovoltaic or electronic applications. Our future work will be concentrated on the measurement of their charge carrier mobilities by TOF technique.

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