A new double-decker phthalocyanine mesogen†‡

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The valence state and the mesomorphic behaviour of a new cerium phthalocyanine double-decker complex bearing thioalkyl substituents are described and spectroscopic studies have revealed that the metal center in this lanthanide double-decker complex is tetravalent making the whole molecule neutral.

With the development during the last few decades of new organic reactions, novel substituted phthalocyanine materials have been successfully prepared and their mesomorphism extensively studied.[1,2] In their liquid crystal phase (mesophase), the large aromatic central cores of the phthalocyanine molecules self-assemble generally into columns of cofacially stacked molecules surrounded by a matrix of molten flexible chains. These columnar macrostructures can either adopt a hexagonal, rectangular, oblique or tetragonal 2D lattice symmetry. Interestingly, the type of lattice symmetry as well as the temperature range of the mesophase can be controlled by careful choice of the substituents and/or the central metal ion. As suggested by Simon *et al*,[3] the similarity between the molecular arrangement of their columnar mesophase and that of a quasi-one-dimensional conducting organic crystal make these molecules good candidates for the preparation of conductive materials with one-dimensional conduction pathways.[4,5] For example, time-of-flight mobilities as fast as $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and electrons, respectively, have indeed recently been reported in the columnar rectangular mesophase of non-peripherally alkylated metal-free phthalocyanine.[6,7]

Unlike metal-free derivatives, lanthanide phthalocyanines are double-decker complexes where the central metal ion is sandwiched between the two phthalocyanine ligands (Scheme 1). The valence state of this compound shows a quite interesting feature. One of these ligands is dianionic whereas the other is radical. As a consequence, this latter is more distorted than the other ring.[8] However on heating, the free electron can delocalise on both rings to make both rings structurally equivalent.[9] As a result, the carrier conduction is generally improved on heating to the mesophase. A fast carrier mobility of $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported for a thioalkylated lutetium phthalocyanine mesogen, which was measured by pulse-radiolysis time resolved microwave conductivity

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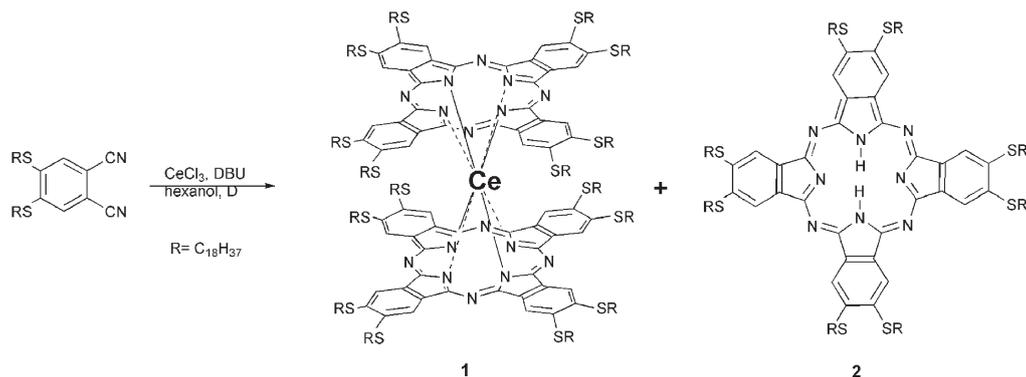*E-mail: yo-shimizu@aist.go.jp; Fax: +81-72-751-9628;*
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‡ Electronic supplementary information (ESI) available: ^{1}H NMR spectrum, X-ray diffraction pattern at 80 and 25 °C, X-ray diffraction data and DSC thermogram of **1**. See DOI: 10.1039/b607851f
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R= alkyl, alkoxy, thioalkyl,...
M= Lu, Eu, Tb,...

Scheme 1 Double-decker phthalocyanine metal complexes.

techniques.[10] In this system, the small HOMO − LUMO gap induced by the weak electronegativity of the thioalkyl chains as well as the large size of the sulfur atom, preventing rotational and translational displacements of the molecules within the core of the columns, play an important role in the fast carrier conduction.[10]

Compared to other lanthanide phthalocyanines,[9–12] rather few substituted cerium phthalocyanine complexes have been reported[13] and to the best of our knowledge their mesogenic properties have never been studied. Interestingly, the cerium atom in those complexes was found to adopt an intermediate valence somewhere between 3 and 4 depending on the electronic nature of the ligand. Therefore, the whole complex can become either neutral or radical depending on the type of tetrapyrrole ring attached to the central metal ion.[13]

In this work, a new thioalkylated double-decker cerium phthalocyanine complex **1**, shown in Scheme 2, was synthesised and its mesomorphism was clarified by DSC, polarised optical microscopy and X-Ray diffraction for the tendency of spontaneous alignment on a substrate.

Compound **1** was synthesised by a modification of the method described by Lee and Ng.[14] In our procedure,¶ a slight excess (~0.5 eq.) of anhydrous cerium trichloride was used to avoid formation of the metal-free derivative **2** (Scheme 2).

Due to the exceptional character of cerium, having an intermediate oxidation state, well-defined NMR signals could be seen in the ^{1}H NMR spectrum of **1**‡ without the addition of a reducing agent such as hydrazine hydrate or $NaBH_4$ normally used with other lanthanide phthalocyanine complexes.[15] The NMR spectrum of **1** was consistent with those of previously reported cerium double-decker structures.[13]

The UV-Vis. absorption spectra of **1** as well as the spectra of its oxidized and reduced derivatives recorded in chloroform are depicted in Fig. 1. The strong Q-band absorption at 687 nm shows

Scheme 2 Preparation of the double-decker cerium phthalocyanine **1**.

a weak shoulder due to the weak π–π interactions occurring between the two phthalocyanine rings. This shoulder disappears completely upon reduction with lithium aluminium hydride due to an increase in the size of the metal ion.[13] The weak absorption at *ca.* 500 nm, generally characteristic of a phthalocyanine radical anion complex,[16] is much weaker compared to other reported substituted cerium double-decker phthalocyanines.[13] However, the intensity of this band significantly increased when iodine was added whereas reduction with LiAlH₄ caused its total disappearance. Moreover, compared to other lanthanide phthalocyanine compounds,[17] no absorption bands in the region 800–900 and 1400–1700 nm corresponding to the π–π transition of a radical phthalocyanine ligand and an intramolecular charge transfer, respectively, were present in the near-IR spectrum of **1**.

These results together with the possibility of obtaining a well-defined ¹H NMR spectrum of **1** suggest that the cerium atom in compound **1** has principally an oxidation state IV. This is interesting as other substituted cerium phthalocyanine complexes with electron donating alkoxy groups were reported to enhance the trivalent character of the cerium center.[13] Since the alkylthio groups are known to be neither electrodonating nor electrowithdrawing groups,[5] the electron in the 4f orbital of the cerium ion can partially delocalise onto the π-orbital of the ligands as in the case of the unsubstituted complex.[18]

The mesomorphism of compound **1** was confirmed by polarised optical microscopy and DSC. Two endothermic peaks at 53 and 119 °C were observed on the heating run of the DSC thermogram
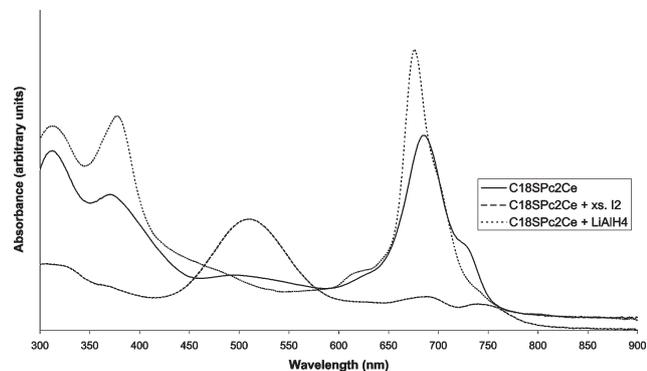
of **1**.‡ These peaks with respective enthalpy values of 364 and 12 kJ mol⁻¹ were assigned to the melting and clearing points of the material. The mesophase temperature range of **1** is wider than those of other lanthanide double-decker compounds having the same ligands.[10]

A fan texture characteristic of a columnar hexagonal mesophase (Col$_h$) was observed by optical microscopy at 116 °C. This texture consisted of some small domain boundaries and some large dark areas seen under crossed polarised light (Fig. 2, top). However, no polydomain formation could be observed on further cooling. On slower cooling (2 °C min⁻¹) hexagonal dendritic growths along with some weak disclinations could be seen under uncrossed polarised light (Fig. 2, bottom). These growths interspersed on further cooling to resemble the isotropic liquid. However, the mesogenic character of this texture was confirmed by the presence of birefringence when the material was smeared. A similar type of texture was found by Ohta *et al.* in the tetragonal mesophase of lutetium phthalocyanine substituted with phenoxy groups.[19] This phenomenon corresponded to a large area where the molecules spontaneously homeotropically align with the substrate.
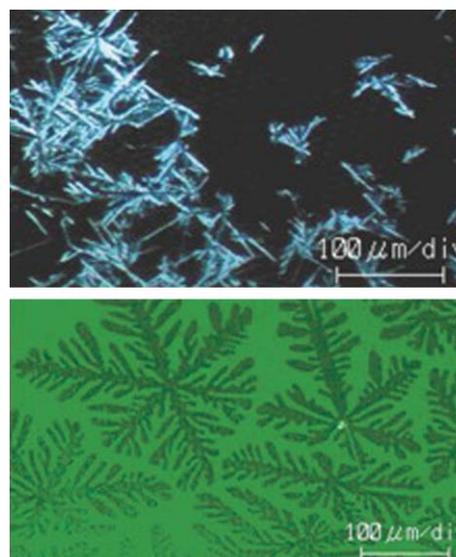

Fig. 2 Optical textures of the Col$_h$ mesophase of **1** at 116 °C (top) and the dendritic growth viewed under uncrossed polarized light at 115 °C (bottom).

Fig. 1 UV-Vis. absorption spectra of **1** in CHCl₃, in the presence of excess iodine and upon addition of LiAlH₄ in CHCl₃/EtOH.

Compound **1** is the first phthalocyanine mesogen with sulfur atoms showing some homeotropic alignment properties on glass substrates. This behaviour makes **1** a good candidate for the measurement of charge carrier mobility by TOF techniques.

Interestingly, microscopic observation also revealed that the homeotropic columnar alignment of **1** could persist down to room temperature (glass transition) without any sign of crystallisation occuring. This tendency of the molecules to keep the same arrangement at low temperature is important for the preparation of single-domain liquid crystalline films required for photovoltaic applications.[20]

Temperature-dependent X-ray diffraction analyses were carried out on compound **1**‡ to determine the lattice symmetry of its mesophase. Six reflections could be detected at 80 °C in the small angle region with a spacing ratio of $1 : 1/\sqrt{3} : 1/2 : 1/\sqrt{7} : 1/3 : 1/4$, respectively. As a result, a hexagonal symmetry was assigned to this mesophase. In the wide angle region, a broad reflection related to the distance between the molten thioalkyl chains and centered at *ca.* 4.6 Å was present whereas no reflections corresponding to the stacking distance between each molecule could be observed. Therefore, the mesophase of **1** was assigned as a hexagonal disordered columnar (Col_{hd}) one.

The six reflections in the small angle region characteristic of a hexagonal columnar arrangement of the molecules were still present in the X-ray pattern of **1** at room temperature.‡ However, the reflection corresponding to the interchain distance was much sharper and now centred at *ca.* 4.2 Å. This indicates that the thioalkyl chains are partially crystallised within the two-dimensional hexagonal packing of the central phthalocyanine cores.[21]

In conclusion, the replacement of the central metal ion in lanthanide phthalocyanine complexes by cerium enhances the thermal stability of the mesophase of these complexes. This could be explained by the unique feature of the cerium phthalocyanine material having two dianionic ligands of equivalent structure. Moreover, the spontaneous alignment of the columnar hexagonal mesophase of this cerium compound and its persistence down to room temperature make this material a good candidate for photovoltaic or electronic applications.

Future work will focus on the measurement of the charge and exciton transport properties of this material by TOF techniques.

Notes and references

¶ Preparation of **1**: 4,5-Bis(octadecylsulfanyl)phthalonitrile (0.6 g, 0.95 mmol) was dissolved in hot hexanol (15 mL) under an atmosphere of nitrogen. Anhydrous cerium(III) trichloride (0.13 mg, 0.53 mmol) and DBU (1 mL, 6.7 mmol) were added to the solution and the reaction mixture was heated at reflux for 4 h. The dark solution was cooled to room temperature and methanol (20 mL) was added to the flask. The dark precipitate was filtered off and washed with cold methanol. The dark solid was then chromatographed over silica gel using a 1 : 1 mixture of hexane/dichloromethane as eluant. Evaporation of the solvent and recrystallisation from ethyl acetate yielded **1** (0.4 g, 59%) as a dark powder; mp 53 and 119 °C (ethyl acetate); Found: C, 73.64; H, 10.59; N, 3.62. $C_{352}H_{608}CeN_{16}S_{16}$ Requires C, 73.94; H, 10.72; N, 3.92%; ν_{max} (KBr)/cm^{-1} 2955, 2923, 2847 (alkyl), 1592 (C=C Ar), 1070 (C–N), 744 (Ar–H), 532 (S–C); δ_H (500 MHz, CDCl$_3$) 8.58 (16H, s, H$_{arom}$), 3.65 (16H, m, Ar–C*H*H–), 3.50 (16H, m, Ar–CH*H*–), 2.08 (32H, m, Ar–CH$_2$–C*H$_2$*–), 1.78 (32H, m, H$_{aliphatic}$), 1.68–1.15 (448H, m, H$_{aliphatic}$), 0.88 (48H, t, *J* 7.0, CH$_3$–); MALDI-MS: cluster at 5716 D (M$^+$, 100%); λ_{max} (abs, log ε/M^{-1} cm^{-1}) 687 (5.2), 494 (4.7), 370 (5.0) and 312 (5.2) nm (CHCl$_3$).

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