

# Chromic Materials. Part 1.—Liquid-crystalline Behaviour and Electrochromism in Bis(octakis-*n*-alkylphthalocyaninato)lutetium(III) Complexes

Tsuyoshi Komatsu,<sup>a</sup> Kazuchika Ohta,\*<sup>a, b</sup> Tetsuya Fujimoto<sup>b</sup> and Iwao Yamamoto<sup>b</sup>

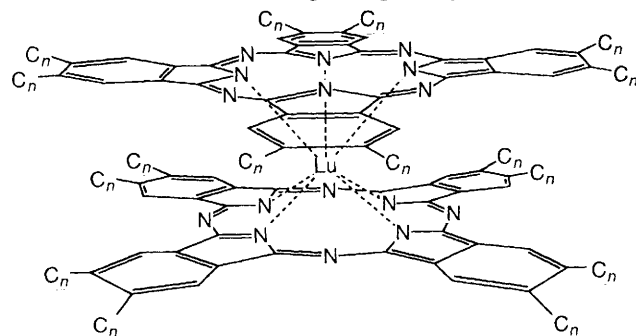
<sup>a</sup> Eastern Co., Ltd., Chino 391, Japan

<sup>b</sup> Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda 386, Japan

Novel bis(phthalocyaninato)lutetium(III) complexes substituted with long *n*-alkyl chains have been synthesized. These complexes, **1a–c**, show three kinds of discotic mesophase ( $D_{hd}$ ,  $D_{ob,d}$  and  $D_L$ ). Also **1a–c** display the three primary colours (red, green, blue) of electrochromism in their solutions. The solutions of oxidized species of **1a–c** are nearly red, although those of conventional bis(phthalocyaninato)lutetium(III) complexes are orange.

Bis(phthalocyaninato)lutetium(III) complex ( $Pc_2Lu$ ) is a multifunctional compound having a sandwich structure and a wide range of applications: intrinsic semiconductivity,<sup>1</sup> electrochromism,<sup>2</sup> third-order optical non-linearity,<sup>3</sup> and so on. Thus, they have been examined for a wide variety of possible applications such as field-effect transistors (FET)<sup>4</sup> and displays.<sup>5</sup> Like many phthalocyanine compounds,  $Pc_2Lu$  complexes are insoluble in most organic solvents. For this reason,  $Pc_2Lu$  complexes substituted with long alkoxymethyl groups were synthesized by Simon and co-workers<sup>6</sup> and the  $Pc_2Lu$  derivatives that are soluble in organic solvents were obtained. These long-chain substituted complexes show discotic mesomorphism<sup>6,7</sup> and electrochromism. These derivatives show three colours (orange, green, blue).<sup>8</sup>

When we synthesized the new  $Pc_2Lu$  complexes substituted with less electron-donating long-*n*-alkyl chains, **1a–c**



$$C_n = C_n H_{2n+1}$$

$$\mathbf{1a} \quad n=8$$

$$\mathbf{1b} \quad n=12$$

$$\mathbf{1c} \quad n=18$$

we expected that the oxidized complex would appear red. The results were that **1a–c** exhibited the following two properties: (1) they displayed the three primary colours (red, green, blue) of electrochromism in solutions; (2) they displayed three kinds of discotic mesophase ( $D_{hd}$ ,  $D_{ob,d}$  and  $D_L$ ). In this paper, we will report on these properties of **1a–c**.

## Experimental

### Synthesis

Synthesis of the bis(octakis-*n*-alkylphthalocyaninato)lutetium(III) complexes, **1a–c**, were carried out according to established methods. First, octakis(*n*-alkyl)phthalocyanine metal-free compounds were synthesized using the method of Ohta *et al.*<sup>9</sup> These compounds were then coordinated with

lutetium(III) using lutetium(III) acetate by the method of Simon and co-workers<sup>6</sup> to afford their corresponding complexes **1a–c**. These complexes were purified by recrystallization from ethyl acetate. They gave satisfactory C, H and N analyses (Table 1), and the structures were confirmed by electronic spectra (Table 2).

### Measurements

Elemental analyses of the complexes **1a–c** were carried out by using a Perkin-Elmer Elemental Analyzer 240B. The UV–VIS spectra were recorded using a Hitachi 330 spectrophotometer. The phase transition behaviour of **1a–c** was observed with a polarizing microscope, Olympus BH-2, equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and 82, and measured with differential scanning calorimeters, a Rigaku Thermoflex TG–DSC and a Rigaku Thermoflex DSC–10A. To establish the mesophases, the powder X-ray patterns were measured with Cu-K $\alpha$  radiation using a Rigaku Geigerflex equipped with a hand-made heating plate controlled by a thermoregulator.<sup>10</sup>

Cyclic voltammograms of **1a–c** in  $CH_2Cl_2$  were obtained using a conventional three-electrode cell and a hand-made cyclic voltammeter. The concentrations of **1a–c** were ca.  $2 \times 10^{-4}$  mol l<sup>-1</sup> in  $CH_2Cl_2$ . For the electrolyte, tetrabutylammonium perchlorate at a concentration of 0.1 mol l<sup>-1</sup> in  $CH_2Cl_2$  was used. The working electrode, the reference electrode and the counter-electrode were a glassy carbon electrode, a saturated calomel electrode and a platinum wire, respectively.

## Results and Discussion

### Solubility

The  $Pc_2Lu$  complexes substituted with long *n*-alkyl chains, **1a–c**, dissolve readily in *n*-hexane, benzene, toluene, chloroform, dichloromethane, diethyl ether, and tetrahydrofuran. On the other hand, they are insoluble in *N,N*-dimethyl formamide, acetonitrile, acetone, methyl alcohol and ethyl alcohol. For recrystallization, ethyl acetate was found to be the optimum solvent.

### Stability

The complexes **1a–c** do not decompose under ordinary light. They are stable for a dc voltage of  $\pm 2.0$  V but decompose beyond  $\pm 3.0$  V.

Table 1 Elemental analysis data of the (C<sub>n</sub>Pc)<sub>2</sub>Lu (n = 8, 12, 18) complexes, 1a–c

compound	M <sub>w</sub>	elemental analysis (%): found (calculated)		
		C	H	N
1a	C <sub>192</sub> H <sub>288</sub> N <sub>16</sub> Lu (2995.50)	76.37 (76.99)	9.87 (9.69)	7.51 (7.48)
1b	C <sub>256</sub> H <sub>416</sub> N <sub>16</sub> Lu (3893.33)	78.87 (78.98)	10.76 (10.77)	5.90 (5.76)
1c	C <sub>352</sub> H <sub>608</sub> N <sub>16</sub> Lu (5239.82)	80.56 (80.69)	11.50 (11.70)	4.25 (4.28)

Table 2 UV–VIS and near-IR absorption spectra data of the (C<sub>n</sub>Pc)<sub>2</sub>Lu (n = 8, 12, 18) complexes, 1a–c, in dichloromethane

compound	concentration/mol dm <sup>−3</sup>	wavelength/nm [ $\lambda_{\text{max}}$ (log $\epsilon$ )]	
1a	1.33 × 10 <sup>−5</sup>	UV–VIS	286 (4.94), 327 (5.15), 351 (5.12), 480 (4.60), 609 (4.61), 648 (sh) (4.52), 676 (5.32) <sup>a</sup>
		near-IR	930 (3.93), ca. 1420 (4.20) <sup>b</sup>
1b	1.09 × 10 <sup>−5</sup>	UV–VIS	287 (4.90), 328 (5.09), 349 (5.07), 478 (4.52), 609 (4.53), 649 (sh) (4.52), 676 (5.23) <sup>a</sup>
		near-IR	930 (3.90), ca. 1435 (4.09) <sup>b</sup>
1c	1.05 × 10 <sup>−5</sup>	UV–VIS	287 (4.92), 328 (5.10), 351 (5.09), 479 (4.55), 608 (4.55), 648 (sh) (4.49), 676 (5.24) <sup>a</sup>
		near-IR	930 (3.89), ca. 1415 (4.12) <sup>b</sup>

<sup>a</sup>Q band. <sup>b</sup>These values are the peaks on a very broad absorption band between 1100 and 1700 nm.

Table 3 Phase transition temperatures (T) and enthalpy changes (ΔH) of the (C<sub>n</sub>Pc)<sub>2</sub>Lu (n = 8, 12, 18) complexes 1a–c

compound	phase <sup>a</sup>	$\xrightarrow[\Delta H/\text{kcal mol}^{-1}]{T/^{\circ}\text{C}}$	phase	relaxation
1a	K	$\xrightarrow[11.3]{79}$	D <sub>hd</sub>	$\xrightarrow[3.3]{82 \text{ (very slow)}}$ iso
1b				
1c				

<sup>a</sup>Phase nomenclature: K = crystal, D<sub>hd</sub> = discotic hexagonal disordered mesophase, D<sub>ob,d</sub> = discotic oblique disordered mesophase, D<sub>L</sub> = discotic lamellar mesophase, and iso = isotropic liquid.

Liquid-crystalline Properties

The phase-transition schemes of 1a–c are shown in Table 3. The assignments of X-ray reflections of each of the mesophases are summarized in Table 4.

1a shows a very narrow temperature range of an enantiotropic discotic hexagonal disordered columnar (D<sub>hd</sub>) mesophase in the range 79–82 °C. It is interesting that 1a is liquid crystalline while *n*-octyloxymethyl-substituted Pc<sub>2</sub>Lu complex is not.<sup>6</sup>

The virgin sample of 1b shows a discotic oblique disordered columnar (D<sub>ob,d</sub>) mesophase at room temperature (rt). This is the first instance of the D<sub>ob,d</sub> mesophase in phthalocyanine compounds. On heating this mesophase, it cleared to isotropic liquid (ISO) at 32 °C, but this ISO soon relaxed into a D<sub>hd</sub> mesophase. This mesophase cleared slowly to ISO at 44 °C. The sample cooled rapidly from ISO gave the D<sub>ob,d</sub> mesophase. When it was heated again, this D<sub>ob,d</sub> mesophase showed similar behaviour to the virgin sample, while the slowly cooled sample from ISO gave the D<sub>hd</sub> mesophase. The phase transition of 1b can be reasonably explained by using a Gibbs energy *versus* temperature (*G–T*) diagram. The schematic *G–T* diagram and the DSC thermogram of 1b are shown in Fig. 1.

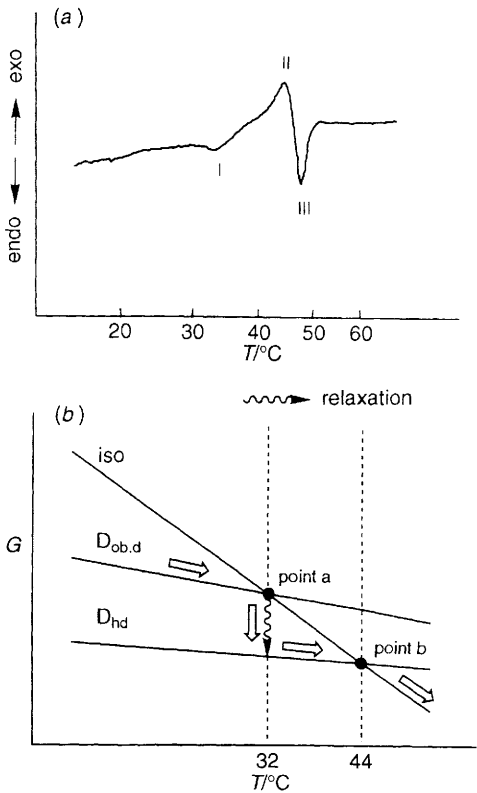


Fig. 1 Differential scanning calorimetry (DSC) thermogram and schematic Gibbs energy versus temperature (*G–T*) diagram for the complex 1b

When the virgin state of the D<sub>ob,d</sub> mesophase was heated (an open arrow on the D<sub>ob,d</sub> line in this *G–T* diagram), it cleared into ISO at the intersection of the D<sub>ob,d</sub> line and the ISO line denoted as point a (32 °C) in the diagram, which corresponds to endothermic peak I in the DSC thermogram. At the same temperature, this ISO relaxed into the D<sub>hd</sub> mesophase which is more stable than the ISO. This relaxation corresponds to exothermic peak II in the DSC thermogram. On further heating, D<sub>hd</sub> mesophase cleared into ISO again at the intersec-

Table 4 X-Ray diffraction data of the (C<sub>n</sub>Pc)<sub>2</sub>Lu (n = 8, 12, 18) complexes 1a–c

compound	mesophase (lattice constant)	spacing/Å		Miller indices (hkl)
		measured	calculated	
1a	D <sub>hd</sub> at 80 °C (a = 25.0 Å)	21.6	21.6	(100)
		12.4	12.5	(110)
		10.8 <sup>a</sup>	10.8	(200)
		ca. 4.5	—	—
		—	—	—
1b	D <sub>ob,d</sub> at rt  $\left[ \begin{matrix} a = 25.7 \text{ Å} \\ b = 22.5 \text{ Å} \\ \gamma = 96^\circ \end{matrix} \right]$	25.7 <sup>a</sup>	25.7	(100)
		18.4	17.9	(110)
		16.1 <sup>a</sup>	16.1	(110)
		12.6	12.9	(200)
		11.2 <sup>a</sup>	11.2	(020)
		10.8	10.7	(120)
		8.67	8.58	(300)
		7.61	7.73	(310)
		6.11	6.17	(230)
		ca. 4.2	—	—
	D <sub>hd</sub> at 42 °C (a = 31.5 Å)	27.3 <sup>a</sup>	27.3	(100)
		15.5	15.8	(110)
		13.4	13.6	(200)
		ca. 4.6	—	—
		—	—	—
1c	D <sub>L</sub> <sup>b</sup> at rt (c = 32.0 Å)	30.3	31.8	(001)
		16.0	15.9	(002)
		10.6 <sup>a</sup>	10.6	(003)
		ca. 4.1	—	—
		—	—	—
	D <sub>hd</sub> <sup>c</sup> at 40 °C (a = 32.9 Å)	28.5	28.5	(100)
		17.4	17.4	(110)
		15.2 <sup>a</sup>	15.2	(200)
		4.3	—	—
		4.1	—	—

<sup>a</sup>The Miller indices of these peaks were assumed to be the standard ones for the indexation. <sup>b</sup>The D<sub>L</sub> mesophase virgin state was obtained by reprecipitation in ethyl acetate at rt. <sup>c</sup>The mesophase was prepared by cooling the iso to 40 °C.

Table 5 Redox potentials (V vs. SCE) and Q-band absorptions (λ<sub>max</sub>/nm) of the (C<sub>n</sub>Pc)<sub>2</sub>Lu (n = 8, 12, 18) complexes, 1a–c, in dichloromethane

compound		redox potential (V vs. SCE) (in 0.1 mol dm <sup>−3</sup> Bu <sub>4</sub> NClO <sub>4</sub> –CH <sub>2</sub> Cl <sub>2</sub> )			
		[(C <sub>n</sub> Pc) <sub>2</sub> Lu] <sup>−</sup> blue	[(C <sub>n</sub> Pc) <sub>2</sub> Lu] <sup>0</sup> green	[(C <sub>n</sub> Pc) <sub>2</sub> Lu] <sup>+</sup> red	
1a	λ <sub>max</sub> /nm	638	−0.17	+0.28	712
1b	λ <sub>max</sub> /nm	636	−0.17	+0.29	712
1c	λ <sub>max</sub> /nm	636	−0.17	+0.28	711
Pc <sub>2</sub> Lu	λ <sub>max</sub> /nm	615	+0.01	+0.44	691 (yellowish green)
(C <sub>12</sub> OPc) <sub>2</sub> Lu	λ <sub>max</sub> /nm	625	−0.18	+0.25	704 (orange)
(C <sub>12</sub> OCH <sub>2</sub> Pc) <sub>2</sub> Lu <sup>a</sup>	λ <sub>max</sub> /nm	631	—	—	704 (orange)

<sup>a</sup>Ref. 9.

tion of the D<sub>hd</sub> line and the ISO line denoted as point b (44 °C) in the diagram, which corresponds to endothermic peak III in the DSC thermogram. It is interesting that while the *n*-dodecyloxymethyl-substituted Pc<sub>2</sub>Lu complex and the *n*-dodecyloxy-substituted Pc<sub>2</sub>Lu complex have only the D<sub>hd</sub> mesophase,<sup>6,7</sup> the present *n*-dodecyl-substituted Pc<sub>2</sub>Lu complex has two columnar mesophases (D<sub>ob,d</sub> and D<sub>hd</sub>). The virgin sample of 1c gave the discotic lamellar (D<sub>L</sub>) mesophase.<sup>11</sup> This is the first example of the D<sub>L</sub> mesophase in phthalocyanine monomers. [It was reported that the

(C<sub>12</sub>OCH<sub>2</sub>)<sub>8</sub>PcSi–O<sub>n</sub> polymer shows a lamellar liquid-crystalline phase<sup>12</sup> and that a planar Pc dimer substituted with twelve 2-ethylhexyloxy side-chains shows a smectic-type mesophase with a nematic order within the lamellar plane.<sup>13</sup>] On heating this D<sub>L</sub> mesophase, it cleared to ISO at 30 °C, but this ISO soon relaxed into a D<sub>hd</sub> phase. This mesophase cleared slowly to ISO at 43 °C. When this ISO was cooled, it consistently produced a mixture of the D<sub>L</sub> and D<sub>hd</sub> phases, unaffected by the cooling speed. For the X-ray diffraction analysis, the broad peak of this D<sub>hd</sub> phase corresponding to

the molten alkyl chains was split into two ( $d=4.3$  Å and  $4.1$  Å). This behaviour may be due to the partial crystallization of alkyl groups similar to the case of *n*-octadecyloxymethyl-substituted  $\text{Pc}_2\text{Lu}$  complex reported by Simon and co-workers ( $d=4.3$  Å and  $4.1$  Å).<sup>6</sup>

From the above results, it can be considered that the discotic mesophase that readily appears in long-chain substituted  $\text{Pc}_2\text{Lu}$  complexes is the hexagonal columnar ( $D_{\text{hd}}$ ) mesophase (Table 3). It is interesting to note that merely by changing the length of the alkyl chains, the long *n*-alkyl substituted  $\text{Pc}_2\text{Lu}$  complexes, **1a–c**, show three kinds of discotic mesophase ( $D_{\text{hd}}$ ,  $D_{\text{ob,d}}$  and  $D_{\text{L}}$ ).

### Electrochromism

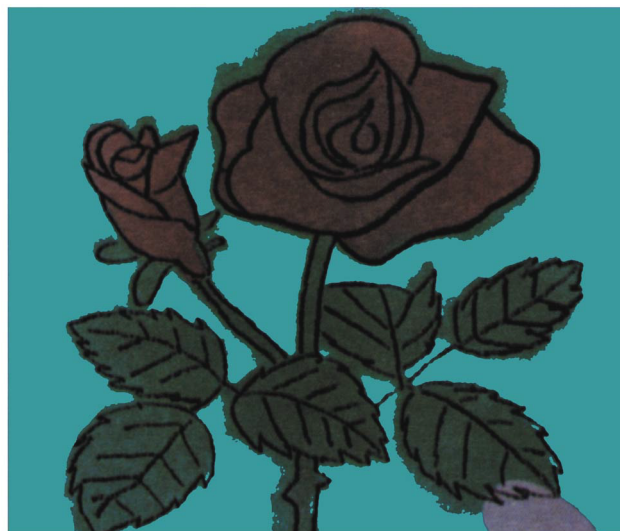
The absorption maximum,  $[\lambda_{\text{max}} (\log \epsilon)]$ , of the electronic spectra of the complexes, **1a–c**, are as summarized in Table 2. **1a–c** exhibited characteristic absorption for  $\text{Pc}_2\text{Lu}$  complexes.<sup>14</sup> The peaks corresponding to the radical species appeared at 478–480 nm and 930 nm. The peak corresponding to intramolecular charge-transfer appeared at *ca.* 1435 nm.

The redox potentials of **1a–c** were determined using cyclic voltammetry (Table 5). The reduction potentials of **1a–c** are all  $-0.17$  V. The oxidation potentials of **1a** and **1c** are  $+0.28$  V and that of **1b** is  $+0.29$  V. These redox potential values have a more negative shift than the unsubstituted  $\text{Pc}_2\text{Lu}$  complex, and are close to the alkoxy-substituted  $(\text{C}_{12}\text{OPc})_2\text{Lu}$  complex.

The electrochromism of **1a–c** was examined. A constant voltage was applied to the  $\text{CH}_2\text{Cl}_2$  solution of **1a–c**, using platinum wires for the working electrode and the counter-electrode, and SCE for the reference electrode. The colour of the solution turned from green to red when  $+1.0$  V was applied, and turned from green to blue when  $-1.0$  V was applied. The wavelengths of the Q-bands of the neutral species, the oxidized species and the reduced species are summarized also in Table 5. The green of the neutral and blue of the reduced species showed no immediately discernible differences when they were compared to those of the core  $\text{Pc}_2\text{Lu}$  complex and the alkoxy-substituted  $(\text{C}_{12}\text{OPc})_2\text{Lu}$  complex. However, the colours of the oxidized species showed a remarkable difference: the alkyl-substituted  $(\text{C}_{12}\text{Pc})_2\text{Lu}$  complex, **1b**, solution was nearly red whereas the unsubstituted  $\text{Pc}_2\text{Lu}$  complex solution was yellowish green; the alkoxy-substituted  $(\text{C}_{12}\text{OPc})_2\text{Lu}$  complex solution and the alkoxymethyl-substituted  $(\text{C}_{12}\text{OCH}_2\text{Pc})_2\text{Lu}$  complex solution were orange.<sup>8</sup> This is supported by the fact that the wavelengths of the Q-band of alkyl-substituted  $(\text{C}_n\text{Pc})_2\text{Lu}$  complexes, **1a–c**, are red-shifted by *ca.* 8 nm more than those of the alkoxy-substituted  $(\text{C}_{12}\text{OPc})_2\text{Lu}$  complex and the alkoxymethyl-substituted  $(\text{C}_{12}\text{OCH}_2\text{Pc})_2\text{Lu}$  complex. Thus, the present alkyl-substituted  $(\text{C}_n\text{Pc})_2\text{Lu}$  complexes, **1a–c**, exhibit the three primary colours (red, green, blue) of electrochromism. A photograph of an electrochromic cell injected with a solution of **1a** ( $0.1 \text{ mol dm}^{-3}$  TBAP) dichloromethane (with  $\pm 1.5$  V applied) is shown in Plate I. Since the response time of this electrochromic cell may be governed by diffusion, each of the colour changes requires several hundred seconds.

### Conclusions

Hexadeca-*n*-alkyl-substituted complexes of bis(phthalocyaninato)lutetium(III) (**1a–c**) have been synthesized. These com-



**Plate I** Photograph of an electrochromic display using a solution of the  $(\text{C}_8\text{Pc})_2\text{Lu}$  complex, **1a**, and  $0.1 \text{ mol dm}^{-3}$  TBAP in dichloromethane between two electrode glass plates

plexes show three kinds of discotic mesophase ( $D_{\text{hd}}$ ,  $D_{\text{ob,d}}$ ,  $D_{\text{L}}$ ), and have oxidation potentials at  $+0.28$  to  $+0.29$  V and reduction potentials at  $-0.17$  V. The complexes, **1a–c**, exhibit the three primary colours (red, green, blue) of electrochromism.

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