Bull. Chem. Soc. Jpn., 76, 781–787 (2003)

Discotic Liquid Crystals of Transition Metal Complexes 33:[#] Spontaneous Uniform Homeotropic Alignment and Unique Mesophase Transition Behavior of Bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)-phthalocyaninato]lutetium(III) Complexes

Kazuaki Hatsusaka, Mutsumi Kimura, and Kazuchika Ohta*

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567

(Received September 24, 2002)

Novel discotic liquid crystalline bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)phthalocyaninato]lutetium(III) complexes, $\{[(C_nO)_2PhO]_8Pc\}_2Lu$ ($n = 12$: **5a** and $n = 13$: **5b**), were synthesized. Their mesomorphic properties were investigated using polarization microscopy, DSC, and temperature-dependent X-ray diffraction techniques. These Lu complexes exhibited a very unique mesophase transition sequence of $Col_h \rightarrow Cub_1 \rightarrow Cub_2 \rightarrow Col_{tet}$. In Col_{tet}, a monodomain spontaneous homeotropic alignment could be achieved. Moreover, they showed two Cub phases, which is the first example of phthalocyanine-based discotic liquid crystals. The electrochemical property of **5a** was also estimated by cyclic voltummetry.

In 1982, Simon and his co-workers pointed out for the first time the application of discotic liquid crystals toward a one-dimensional conductor.[2] Recently, some discotic liquid crystals having a one-dimensional columnar structure show very fast mobility of charge carriers.[3] The conduction in discotic liquid crystals is attributable to hole hopping through the discotic molecules in columns.[4] Both defects and polydomain boundaries in a discotic liquid crystal introduced between two substrates may interrupt the pass and prevent charge carrier transport in the columns. If a discotic liquid crystal does not have any defects or polydomains, it can show much faster mobility of the charge carriers.[5] When discotic liquid crystals are applied to a practical solar cell as transport materials, it will be necessary to form a large-area-uniform monodomain.[4] Thus, the molecular alignment is significant to increase the mobility of discotic liquid crystals for practical usage.

Recently, we found that a neutral radical bis(2,3,9,10,16,17,-23,24-octakisdodecylthiophthalocyaninato)lutetium(III) complex (abbreviated as $[(C_{12}S)_8Pc]_2Lu$, **3** in Fig. 1) shows a very fast mobility of charge carriers, 0.7 cm^2 V^{-1} s^{-1}.[6] It may be attributed to hopping of the radical electron between two Pc macrocycles of the $[(C_{12}S)_8Pc]_2Lu$ complex. Hence, it is rational that the charge transport of such a radical double-decker Lu complex is faster than the corresponding non-radical single-decker Cu complex. If the bis(phthalocyaninato)lutetium(III) analogues would show a spontaneous uniform homeotropic alignment without defects, much faster mobility of the charge carrier could be achieved. However, such a perfect spontaneous homeotropic alignment could not be realized for the previous double-decker Lu complexes: **1**,[7] **2**,[8] and **3**[6] (Fig. 1). On the other hand, our recently synthesized octakis(bisalkoxyphenoxy)-group-substituted Cu complexes, **4a–d** (abbreviated as $[(C_nO)_2PhO]_8PcCu$; $n =$ 11–14), showed a perfect spontaneous homeotropic alignment in the Col_{tet} mesophase.[5] If novel double-decker Lu complexes, bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)-phthalocyaninato]lutetium(III) (**5a** and **5b**: abbreviated as $\{[(C_nO)_2PhO]_8Pc\}_2Lu$ ($n = 12$ and 13)), could be synthesized by using the previous $[(C_nO)_2PhO]_8PcH_2$ ligand, the discotic liquid crystals would have both properties of a perfect spontaneous homeotropic alignment and very fast mobility of the charge carriers. Hence, novel double-decker Lu complexes, **5a**,**b** were synthesized.

We wish to report here that the present novel sandwich complexes, **5a**,**b**, show a monodomain spontaneous homeotropic alignment in the Col_{tet} mesophase, and a very interesting mesophase transition sequence.

Experimental

1. Synthesis. The synthetic route is shown in Scheme 1. The dicyanobenzene derivatives **7** were prepared by a previously reported method.[5] The bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)phthalocyaninato]lutetium(III) complexes, **5**, were synthesized by an improved method of Belarbi et al.[9] The detailed procedures for a representative complex **5a**, $\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$, are described as follows:

$\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$ (5a). 4,5-Bis(3,4-didodecyloxyphenoxy)-1,2-dicyanobenzene, **7a**, (0.500 g, 0.476 mmol) was dissolved in 1-hexanol (5 mL). To the solution, DBU (3 drops) and lutetium(III) acetate tetrahydrate (0.0252 g, 0.0595 mmol) were added. The mixture was then refluxed for 49 hours under a nitrogen atmosphere. After cooling to room temperature, the reaction solution was poured into 300 mL of methanol. The target product precipitated as a dark-green solid. The solution on the precipitated solid was removed by a pipette. The wet solid was gently blown by dry nitrogen gas until it dried completely, and then solid–liquid extraction was performed using ethanol (70 mL) seven times to remove the by-products. The

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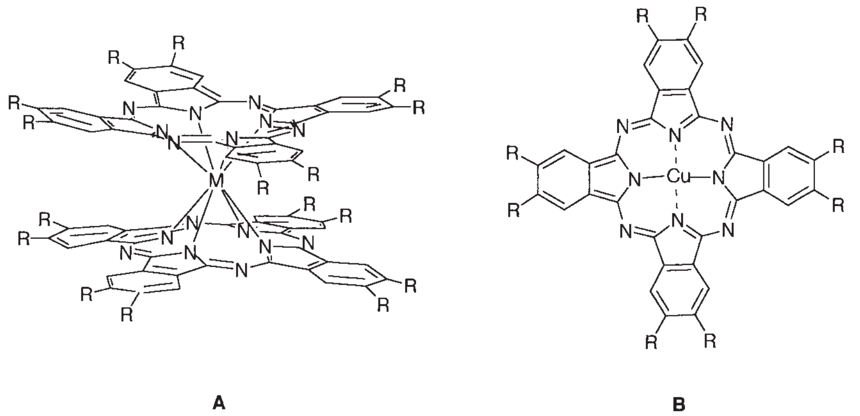
[#] Part 32. Ref. 1.



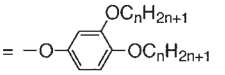
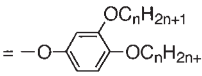
1	A; R = $C_{12}H_{25}OCH_2$; M=Lu	$[(C_{12}OC)_8Pc]_2Lu^a$
2	A; a: R = $C_{12}H_{25}O$; M=Nd, Eu, Er, Lu	$[(C_nO)_8Pc]_2M^b$
	b: R = $C_{10}H_{21}O$; M=Er	
	c: R = $C_{18}H_{37}O$; M=Er	
3	A; R = $C_{12}H_{25}S$; M=Lu	$[(C_{12}S)_8Pc]_2Lu^c$
4	B; R =  $-O-C_6H_3(OC_nH_{2n+1})_2$	$[(C_nO)_2PhO]_8PcCu$: Singledecker[d]
	a: n=11 c: n=13	
	b: n=12 d: n=14	
5	A; R =  $-O-C_6H_3(OC_nH_{2n+1})_2$; M=Lu	$\{[(C_nO)_2PhO)_8Pc]\}_2Lu$: Doubledecker
	a: n=12 b: n=13	(This work)
6	A; R =H	Pc_2M^e
	a: M=Lu c: M=Tm	
	b: M=Yb d: M=Dy	

Fig. 1. Formulae of bis(phthalocyaninato)lanthanoid(III) derivatives **1**, **2**, **3**, **5**, **6** and octakis(dialkoxyphenoxy)phthalocyaninatocopper(II) derivatives **4**. Refs. **a**: 7); **b**: 8); **c**: 6); **d**: 5); **e**: 21).

crude product was purified by column chromatography (silica gel, $CHCl_3$; $R_f = 1.00$ and then silica gel, *n*-hexane:THF = 95:5; $R_f = 0.48$), and by gel-permination chromatography (Bio-beads, SX-1, THF) to give 0.113 g of dark green solid. Yield: 20%.

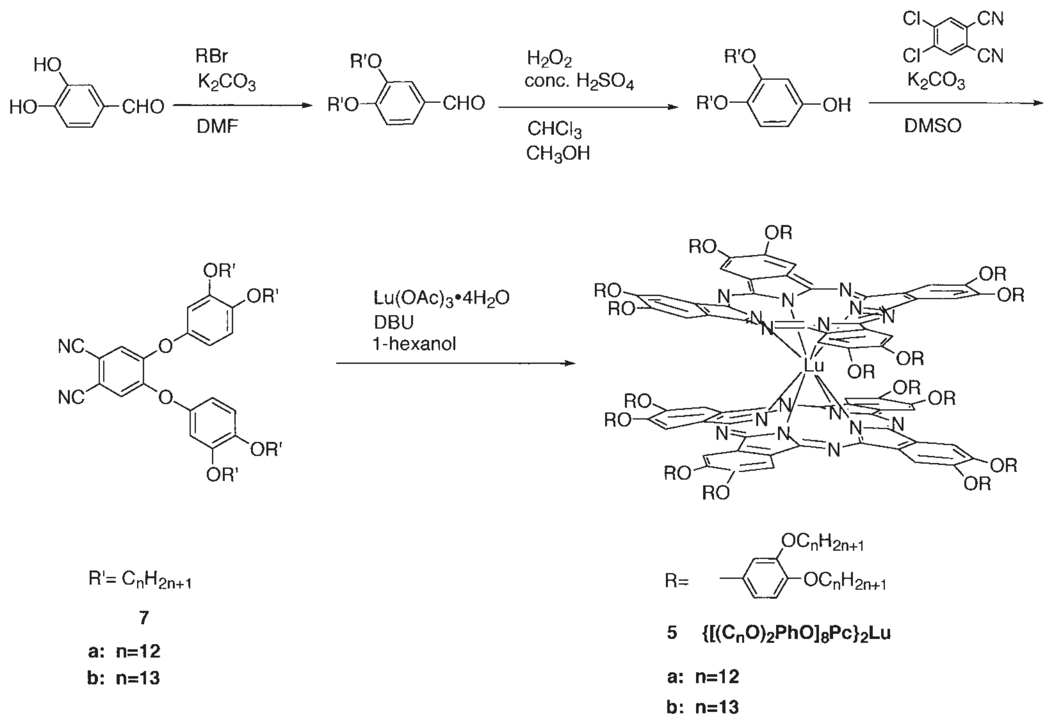
5a: Elemental Analysis. Found: C, 76.38; H, 10.56; N, 2.73%. Calcd for $C_{544}H_{864}N_{16}O_{48}Lu$: C, 76.23; H, 10.16; N, 2.61%. UV-vis spectrum in $CHCl_3$ (6.59×10^{-6} mol/L) nm (log ε), 674 (5.30), 644(sh) (4.71), 608 (4.65), 460(sh) (4.60), 353 (5.13), 328 (5.14), 288 (5.16); MALDI-TOF MS, found (calculated) m/z 8572.0 (8572.0).

5b: Elemental analysis. Found: C, 76.30; H, 10.74; N, 2.56%. Calcd for $C_{576}H_{928}N_{16}O_{48}Lu$: C, 76.69; H, 10.37; N, 2.48%. UV–vis spectrum in $CHCl_3$ (6.61×10^{-6} mol/L) nm (log ε), 674 (5.14), 644(sh) (4.60), 609 (4.52), 460(sh) (4.51), 351 (5.05), 328 (5.08), 288 (5.14); MALDI-TOF MS, found (calculated) m/z 9020.6 (9020.9).

2. Measurements. The present phthalocyanine derivatives, **5a**,**b**, were identified by elemental analysis (Perkin-Elmer elemental analyzer 2400), electronic absorption spectroscopy (Hitachi U-4100 spectrophotometer) and MALDI-TOF Mass Spectroscopy (Perseptive Boisystem Voyager). The phase transition behavior of these compounds was observed by using a polarizing microscope (Olympus BH2), equipped with a heating plate controlled by a thermoregulator (Mettler FP80 hot stage, Mettler FP82 Central Processor), and measured by a differential scanning calorimeter (Shimadzu DSC-50). X-ray diffraction measurements were performed with Cu-Kα radiation by using a Rigaku RAD X-ray diffractometer equipped with a hand-made heating plate[10,11] controlled by a thermoregulator. The redox potential of **5a** was measured by an electrochemical analyzer (ALS Model 600A).

Results and Discussion

1. Mesomorphism. 1-1. Phase Transition Behavior. The phase transition temperatures and enthalpy changes of the $\{[(C_nO)_2PhO]_8Pc\}_2Lu$ (n = 12 and 13: **5a** and **5b**) complexes



R'= C_nH_{2n+1}

7

a: n=12

b: n=13

R=

5 **{[($C_nO)_2PhO]_8Pc\}_2Lu$**

a: n=12

b: n=13

Scheme 1. Synthetic route to the bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)phthalocyaninato]lutetium(III) complexes **5a**,**b**. DBU = 1,8-diazabicyclo[5.4.0]-7-undecene.

Table 1. Phase Transition Temperatures and Enthalpy Changes of the $\{[(C_nO)_2PhO]_8Pc\}_2Lu$ (n = 12 and 13) Derivatives

Compound $\{[(C_nO)_2PhO]_8Pc\}_2Lu$	Phase $\xrightarrow{T/^\circ\mathrm{C}\ [\Delta H/\mathrm{kJ\,mol^{-1}}]^{a)}}$ phase$^{b)}$ $\rightsquigarrow$ relaxation
5a: n = 12	$\begin{tikzcd} \mathrm{K}_2 \arrow[r, "35"] \arrow[rr, bend left, "40\text{ - }60"] & \mathrm{Col_h\,(v)} \arrow[r, shift left, "139\ [24]"] \arrow[dl, shift left] & \mathrm{Cub_I} \arrow[l, shift left] \arrow[r, shift left, "164\ [15]"] \arrow[dr, "205^b"'] & & \mathrm{Cub_2} \arrow[ll, shift left] \arrow[r, shift left, "216\ [7]"] \arrow[dr, "229\ [1]"'] & & \mathrm{Col_{tet}} \arrow[ll, shift left] \arrow[r, shift left, "239\ [7]"] & \mathrm{I.L.} \arrow[l, shift left] \\ \mathrm{K_1} \arrow[ur, shift left, "0\ [177]"] & & & \mathrm{I.L.} \arrow[ur, rightsquigarrow] & & \mathrm{I.L.} \arrow[ur, rightsquigarrow] & & \end{tikzcd}$
5b: n = 13	$\begin{tikzcd} \mathrm{K_2\,(v)} \arrow[r, "31"] \arrow[rr, bend left, "116"] & \mathrm{Col_h} \arrow[r, shift left, "122\ [17]"] \arrow[dl, shift left] & \mathrm{Cub_I} \arrow[l, shift left] \arrow[r, shift left, "143\ [11]"] \arrow[dr, "188^b"'] & & \mathrm{Cub_2} \arrow[ll, shift left] \arrow[r, shift left, "166\ [8]"] \arrow[dr, "213\ [15]"'] & & \mathrm{Col_{tet}} \arrow[ll, shift left] \arrow[r, shift left, "222\ [2]"] & \mathrm{I.L.} \arrow[l, shift left] \\ \mathrm{K_1\,(v)} \arrow[ur, shift left, "15\ [177]"] & & & \mathrm{I.L.} \arrow[ur, rightsquigarrow] & & \mathrm{I.L.} \arrow[ur, rightsquigarrow] & & \end{tikzcd}$

a) Abbreviations: T = phase transition temperature (°C), ΔH = enthalpy change (kJ mol^{-1}). b) Phase nomenclature: K = crystal, Col$_h$ = hexagonal columnar mesophase, Cub = cubic mesophase, Col$_{tet}$ = tetragonal columnar mesophase, I.L. = isotropic liquid. v = virgin state. [b]This c.p. could be observed not by the DSC measurements, but only by the microscopic observation.

are summarized in Table 1. These phase transition behaviors were established by microscopic observations and differential scanning calorimetry (DSC) measurements. Immediately after purification, the virgin state was a supercooled Col$_h$ for **5a**; it was a mixture of supercooled crystal K_1 and crystal K_2 for **5b**. However, except for this point, both **5a** and **5b** gave the same phase transition behavior. Hence, the detailed phase transition behavior is described for representative complex **5a** in the following.

When a virgin sample was cooled from r.t. to −100 °C and then heated, an endothermic peak was observed at 0 °C by DSC measurements during the heating. The phase transition enthalpy change was 177 kJ/mol. It is larger than that of a phase transition from a crystal to a liquid crystal of the metal free octakis(dodecyloxy)phthalocyanine complex, 122 kJ/mol.[12] The enthalpy difference may have resulted from the number of peripheral alkoxy groups in those complexes. The present double-decker Lu complex **5a** has twice as many alkoxy chains as the metal free octakis(dodecyloxy)phthalocyanine single-decker complex. Therefore, the bigger enthalpy change is also attributable to the phase transition from crystal K_1 to the Col_h mesophase. Upon further heating, another endothermic peak could be observed at 139 °C. This peak corresponds to the phase transition form Col_h to Cub_1. As can be seen from Table 1, the phase transitions over the Col_h phase show $Cub_1 \rightarrow Cub_2 \rightarrow Col_{tet} \rightarrow$ I.L. Additionally, two clearing points were observed at 205 °C and 229 °C between $Cub_1 \rightarrow Cub_2$ and $Cub_2 \rightarrow Col_{tet}$, respectively. The clearing of Cub_1 at 205 °C could not be detected by DSC measurements, but could be repeatedly detected by microscopic observations. Furthermore, it was also detected by microscopic observations that the isotropic liquid resulted from the clearing of Cub_1 relaxed to Cub_2 after a few minutes. Upon further heating, another clearing of Cub_2 could be observed at 229 °C both by DSC measurements and microscopic observations. It was also revealed by microscopic observations that the I.L. resulted from the clearing of Cub_2 relaxed to Col_{tet} after a few minutes. Upon further heating, the highest temperature mesophase Col_{tet} cleared into I.L. at 239 °C. When the I.L. over 239 °C was cooled to −100 °C, the phase transition behaviors changed as shown by the reverse arrows in the Table 1, and finally the K_1 phase appeared. On the other hand, when the I.L. over 239 °C was cooled to r.t., the supercooled Col_h phase appeared, which was confirmed by X-ray diffraction studies. The supercooled Col_h had been left at r.t. for six months, it gave a small endothermic peak at 35 °C for the DSC measurement together with a large endothermic peak of the phase transition from K_1 to Col_h at 0 °C. This apparently indicates that the Col_h phase at r.t. very slowly relaxed into another crystal, K_2. The relaxation from Col_h to K_2 for another compound, **5b**, was more discernible, which supports the relaxation of **5a**. When K_2 of **5a** was heated, it transformed mainly into Col_h at 35 °C, and partially into Cub_1 (by superheating) at 40–60 °C, which was observed as a broad endothermic peak for DSC.

It has not yet been clarified why two Cub phases appear between the high-symmetry Col_h mesophase and the low-symmetry Col_{tet} mesophase. The present compounds, **5a**,**b**, are the second examples of the Cub phase in phthalocyanine derivatives. The previous single-decker $[(C_nO)_2PhO]_8PcCu$ ($n = 11$, 12, 13 and 14) complexes, **4a–d**, are the first examples, as far as we know.[5] However, the present double-decker Lu complexes are the first phthalocyanine derivatives exhibiting two different Cub phases.

1-2. Identification of Mesophases. The X-ray data of all the mesophases of both compounds **5a** and **5b** are listed in Table 2. As can be seen from Table 1, they showed the same mesophases. Hence, the identification of these mesophases was described only for a representative **5a**.

Col_h: The mesophase at r.t. could be identified as a hexagonal columnar mesophase, Col_h. As can be seen from Table 2, the spacings of 36.0, 20.9, 17.8 and 13.7 Å, were in a ratio of $1:1/\sqrt{3}:1/2:1/\sqrt{7}$, which is characteristic for a Col_h mesophase.

The interval of the double-decker complexes gave a stacking distance (h) at about 10.1 Å. The typical van der Waals radius of aromatic compounds is 3.4 Å.[13] The normal face-to-face stacking distance of single-decker phthalocyanine compounds is also 3.2–3.5 Å.[14] Therefore, the face-to-face stacking distance of double-decker phthalocyanine rare-earth metal sandwich complexes may appear at ca. 7 Å. Actually, the stacking distances between double-deckers have been reported at ca. 7–8 Å for discotic liquid crystalline bis(phthalocyaninato)lutetium(III) complexes.[6,7,9,12,15] However, the present double-decker **5a** gave a quite large stacking distance, 10.1 Å. This stacking distance is larger than those of other previously reported bis(phthalocyaninato)-lutetium(III)-based complexes. The reason may be attributed to a large steric hindrance of the eight peripheral phenoxy groups of the present double-decker. These phenoxy groups bonded to the phthalocyanine central cores by ether group may prevent the cores from rotating freely in the columns, so that the thickness of the double-decker may become larger than the usual one. This may result in a longer stacking distance ($h \approx 10.1$ Å) of the double-decker complex. The number of molecules (Z) in a slice of the 2D hexagonal lattice for Col_h is normally one. Therefore, the present stacking distance, 10.1 Å, should be confirmed by a calculation of the Z value. The Z value can be calculated from

$$Z = \rho VN/M, \tag{1}$$

where ρ represents the density of the liquid crystal, N is Avogadro's constant and M is the molecular weight. As listed in Table 2, the two-dimensional (2D) hexagonal lattice constant of **5a** is 41.6 Å. Hence, the volume of a slice of the 2D hexagonal lattice can be calculated from

$$\begin{aligned} V &= a^2 \times \sin 60^\circ \times h = (41.6\ \text{Å})^2 \times \sqrt{3}/2 \times 10.1\ \text{Å} \\ &= 1.51 \times 10^{-20}\ \text{cm}^3. \end{aligned} \tag{2}$$

If the density of the liquid crystals is assumed to be 1.00 g/cm,[3,16,17] the Z in the slice can be calculated from

$$\begin{aligned} Z &= (1.00\ \text{g cm}^{-3} \times 1.51 \times 10^{-20}\ \text{cm}^3 \times 6.02 \times 10^{23}\ \text{mol}^{-1}) \\ &\div 8572.01\ \text{g mol}^{-1} = 1.1 \approx 1. \end{aligned} \tag{3}$$

Therefore, the stacking distance (10.1 Å) is consistent with the distance for the Col_h mesophase. Thus, this phase can be assigned as a Col_h mesophase.

Cub: Two different kinds of temperature-dependent X-ray diffraction patterns could be obtained in the temperature regions between the Col_h and Col_{tet} mesophases, as can be seen from Table 2. All of the spacings of the both phases could be assigned not to the reflections from any 2D lattices of the columnar mesophases, but to the reflections from a 3D cubic lattice very well. These two phases are optically isotropic under a polarizing microscope. Therefore, each of them could be identified as a cubic phase, Cub. The lower-temperature and higher-temperature Cub phases were denoted as Cub_1 and Cub_2, respectively. The types of cubic structures are roughly divided into "spherical association balls" and "bicontinuous aggregated columns".[18] It is very unlikely that such big disk-like molecules of the phthalocyanine-based compound would form a spherical association. Hence, the type of the present two Cub phases may have bicontinuous aggregated columns forming a network (see Fig. 2), although the difference between these two Cub phases is not clear at the present time. Further studies are necessary to clarify it.

Col_{tet}: The highest temperature mesophase at 235 °C could be identified as a tetragonal columnar mesophase, Col_{tet}. Two reflections appeared in the lower angle region. As summarized in Table 2, these spacings are in a ratio of $1\sqrt{2}:1/2$, which is characteristic of a 2D tetragonal columnar mesophase. The stacking distance of the double-decker complex in the columns, h,

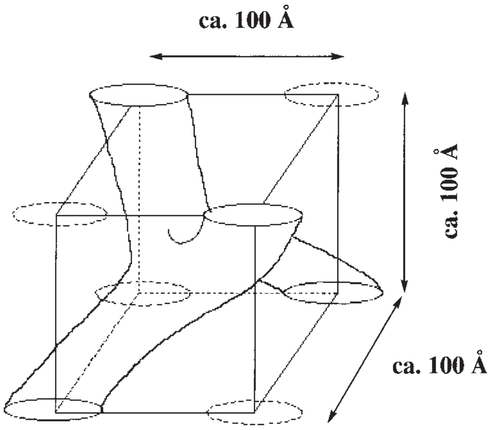
Table 2. X-ray Data of the $\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$ and $\{[(C_{13}O)_2PhO]_8Pc\}_2Lu$ Derivatives

Compound (mesophase)	Lattice constant/Å	Spacing/Å Observed	Spacing/Å Calculated	Miller indices ($h\ k\ l$)
5a: $\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$				
Col_h at r.t.	$a = 41.6$	36.0	36.0	(100)
	$h \approx 10.1$	20.9	20.8	(110)
	$Z = 1.1$ for $\rho = 1.00$	17.8	18.0	(200)
		13.7	13.6	(210)
		ca. 10.1	—	h
		ca. 4.4	—	#
		33.7	33.7	(220)
Cub_1 at 150 °C	$a = 95.3$	28.8	28.7	(311)
	$h \approx 9.3$	27.5	27.5	(222)
	$Z = 61$ for $\rho = 1.00$	ca. 9.3	—	h
		ca. 4.7	—	#
		31.7	31.7	(220)
Cub_2 at 185 °C	$a = 89.7$	28.3	28.4	(310)
	$h \approx 9.0$	25.9	25.9	(222)
	$Z = 51$ for $\rho = 1.00$	ca. 9.0	—	h
		ca. 4.7	—	#
Col_{tet} at 235 °C	$a = 40.0$	28.3	28.3	(110)
	$h \approx 9.7$	20.0	20.0	(200)
	$Z = 1.1$ for $\rho = 1.00$	ca. 9.7	—	h
		ca. 4.7	—	#
5b: $\{[(C_{13}O)_2PhO]_8Pc\}_2Lu$				
Col_h at 56 °C	$a = 39.6$	34.3	34.3	(100)
	$h \approx 9.9$	19.5	19.8	(110)
	$Z = 0.90$ for $\rho = 1.00$	13.0	13.0	(210)
		ca. 9.9	—	h
		ca. 4.2	—	#
Cub_1 at 135 °C	$a = 97.0$	33.8	34.3	(220)
	$h \approx 9.6$	31.0	30.7	(310)
	$Z = 61$ for $\rho = 1.00$	29.4	29.2	(311)
		ca. 9.6	—	h
		ca. 4.6	—	#
Cub_2 at 161 °C	$a = 92.9$	32.7	32.8	(220)
	$h \approx 9.4$	29.4	29.4	(310)
	$Z = 54$ for $\rho = 1.00$	26.9	26.8	(222)
		17.9	17.9	(333)
		ca. 9.4	—	h
		ca. 4.7	—	#
Col_{tet} at 190 °C	$a = 41.1$	29.0	29.0	(110)
	$h \approx 9.1$	20.9	20.5	(200)
	$Z = 1.0$ for $\rho = 1.00$	ca. 9.1	—	h
		ca. 4.9	—	#

Halo of the molten alkoxy chains.

could be observed at around 9.7 Å. When this stacking distance was used, the number of molecules in a slice, Z, could be calculated to be 1.1. It is compatible with the usual number ($Z = 1$) for the Col_{tet} mesophase. In addition, this mesophase gave a cross-shaped dendric natural texture (Fig. 3A), which was optically isotropic. The natural texture clearly reflects a four-fold axis of the 2D-tetragonal symmetry, thus supporting that this phase is a Col_{tet} phase. There have been no reports of the cross-dendric natural texture having a four-fold axis of symmetry, except for in our previous work.[19] Thus, the mesophase could be assigned to Col_{tet} from both a temperature-dependent X-ray structural analysis and polarizing microscopic observations.

1-3. Spontaneous Homeotropic Alignment. As shown in Fig. 3A, the optically isotropic cross-shaped dendric texture appeared when the isotropic liquid had been cooled from 245 °C to 235 °C, and then left at 235 °C for 30 minutes. Upon further holding at this temperature, the cross-shaped dendrites grew very slowly. Part of the isotropic liquid could be long observed among



Bird's-eye View

Side View

Fig. 2. Schematic model of a Cub mesophase forming bicontinuous aggregated structure by discotic molecules.

the dendrites even after 7 hours, as shown in Fig. 3B. After 9 hours, part of isotropic liquid disappeared and, an almost, perfect homeotropic alignment could be achieved (Fig. 3C).

Although the rate of the change from isotropic liquid to $\mathrm{Col_{tet}}$ is very slow, the present compounds, **5a**,**b**, thus form a defect-free monodomain spontaneous homeotropic alignment in the $\mathrm{Col_{tet}}$ mesophase. Such a monodomain spontaneous homeotropic alignment can also be achieved for the previous single-decker copper(II) complex **4**. Hence, it is dependent on not the central metal, but the peripheral octakis(bisalkoxyphenoxy)-group to obtain a monodomain spontaneous homeotropic alignment. As already mentioned, because the conduction in discotic liquid crystals is attributable to hole hopping through the discotic molecules in columns, a uniform alignment of discotic liquid crystals is essential for a much faster mobility of charge carriers. The present compounds, **5a**,**b**, exhibited a spontaneous uniform homeotropic alignment for the first time in discotic liquid crystalline phthalocyanine double-decker complexes. Therefore, the present compounds, **5a**,**b**, have excellent paths for charge carrier transportation. Except for the $\mathrm{Col_{tet}}$ mesophase, however, the spontaneous uniform homeotropic alignment does not occur in any mesophases or crystal phases. In order to use discotic liquid crystals as practical applications, like solar cells, in the future, it is more desirable that a spontaneous uniform homeotropic alignment occurs at r.t. If a uniform homeotropic alignment of discotic liquid crystals could be fixed by the polymerization of discotic liquid crystals, it would be realized even at r.t.

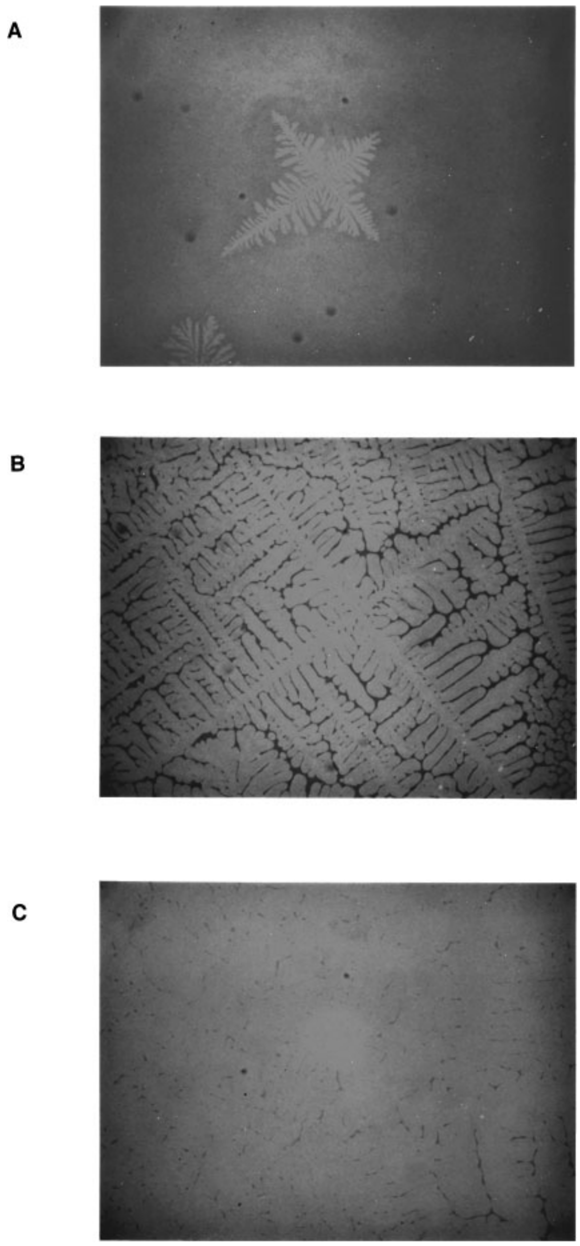


Fig. 3. Photomicrographs of $\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$ (**5a**) at 235 °C, recorded with uncrossed polarizers; **A**: after 30 minutes, **B**: after 7 hours, **C**: after 9 hours.

2. Redox Potential. The conductivity (σ) of materials is related to the concentration (n) of charge carriers and to the mobility (μ) by

$$\sigma = ne\mu,$$

where $e = 1.6 \times 10^{-19}$ Coulomb.[20] In the case of intrinsic semiconductive molecules, the generation of charge carriers may be represented by the reaction

$$\mathrm{AAA} \longleftrightarrow \mathrm{A^+A^-A} \quad \text{free carriers,}$$

where A is a molecular unit.[20]

The ion pair A^+A^- is thermally or photochemical generated, and the activation energy for its formation may be estimated from the redox potentials of the molecular units in solution.[20] Therefore, it can be considered that the conductivity is estimated by the redox potential. The redox potentials of the non-substituted core bis(phthalocyaninato)lutetium(Ⅲ) complex (**6a**)[20] and lithium phthalocyaninate were reported to be 0.48 and 0.83 V, respectively.[20] Both complexes are intrinsic semiconductors. On the other hand, the redox potential of the present Lu complex, $\{[(C_{12}O)_2PhO]_8Pc\}_2Lu$ (**5a**), is $\Delta E_{\text{redox}} = E_{1/2}{}^{\text{ox}} - E_{1/2}{}^{\text{red}} = 0.21\ \text{V} - (-0.36\ \text{V}) = 0.57\ \text{V}$ (in 0.1 M CH_2Cl_2 solution with tetrabutylammonium perchlorate; vs saturated calomel electrode). Accordingly it can be expected that the present Lu complexes, **5a**,**b**, may become intrinsic semiconductors, although the bulky phenoxy groups in the periphery may prevent a π–π overlap of the central core. Since **5a**,**b** show a monodomain spontaneous homeotropic alignment in the Col_{tet} mesophase, very high mobility can also be expected in this mesophase.

Conclusion

Novel discotic liquid crystalline bis[2,3,9,10,16,17,23,24-octakis(3,4-dialkoxyphenoxy)phthalocyaninato]lutetium(Ⅲ) complexes, $\{[(C_nO)_2PhO]_8Pc\}_2Lu$ ($n = 12$: **5a** and $n = 13$: **5b**) were synthesized. These double-decker Lu complexes show a very unique mesophase transition sequence of $\text{Col}_\text{h} \rightarrow \text{Cub}_1 \rightarrow \text{Cub}_2 \rightarrow \text{Col}_{\text{tet}}$ during the heating stage. According to our expectation, the Lu complexes exhibit a monodomain spontaneous homeotropic alignment in Col_{tet}. Unexpectedly, they exhibit two Cub phases, which are the first examples in phthalocyanine-based discotic liquid crystals. The present Lu complexes may become intrinsic semiconductors, because the redox potential, ΔE_{redox}, is 0.57 V.

This work was partially supported by a Grant-in-Aid for Priority Area Research (12129205) by the Ministry of Education, Science, Sports and Culture.

References

1 Part 32: T. Nakai, K. Ban, K. Ohta, and M. Kimura, *J. Mater. Chem.*, **12**, 844 (2002).

2 C. Piechoki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, **104**, 5245 (1982).

3 K. Ohta, *Ekisho*, **6**, 13 (2002).

4 J. Hanna, *Oyobuturi*, **68**, 26 (1999).

5 K. Hatsusaka, K. Ohta, I. Yamamoto, and H. Shirai, *J. Mater. Chem.*, **11**, 423 (2001).

6 K. Ban, K. Nishizawa, K. Ohta, A. M. van de Craats, J. M. Warman, I. Yamamoto, and H. Shirai, *J. Mater. Chem.*, **11**, 321 (2001).

7 C. Piechoki, J. Simon, J.-J. André, D. Guillon, P. Petit, A. Skoulios, and P. Weber, *Chem. Phys. Lett.*, **122**, 124 (1985).

8 J. Sleven, C. Görller-Walrand, and K. Binnemans, *Mater. Sci. Eng., C.*, **18**, 229 (2001).

9 Z. Belarbi, C. Sirlin, J. Simon, and J.-J. André, *J. Phys. Chem.*, **93**, 8105 (1989).

10 H. Ema, Master Thesis, Shinshu University, Ueda, Japan (1988), Chap. 7.

11 H. Hasebe, Master Thesis, Shinshu University, Ueda, Japan (1991), Chap. 5.

12 A. M. van de Craats, J. M. Warman, H. Hasebe, R. Naito, and K. Ohta, *J. Phys. Chem. B.*, **101**, 9224 (1997).

13 J. Simon and P. Bassoul, "Phthalocyanines Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, Wiley-VCH, New York (1995), p. 242, and references cited therein.

14 K. Ban, K. Nishizawa, K. Ohta, and H. Shirai, *J. Mater. Chem.*, **10**, 1083 (2000).

15 R. Naito, K. Ohta, and H. Shirai, *J. Porphyrins Phthalocyanines.*, **5**, 44 (2001).

16 K. Praefcke, A. Levelut, B. Kohne, and A. Eckert, *Liq. Cryst.*, **6**, 263 (1989).

17 K. Saito and M. Sorai, *Ekisho*, **5**, 21 (2001).

18 C. E. Fairhurst, S. Fuller, J. Gray, M. C. Holmes, and G. J. T. Tiddy, "Handbook of Liquid Crystals," ed by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, Wiley-VCH, New York (1998), p. 341, and references cited therein.

19 K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto, and N. Kobayashi, *J. Mater. Chem.*, **8**, 1979 (1998).

20 J. Simon and P. Bassoul, "Phthalocyanines Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, Wiley-VCH, New York (1995), p. 223, and references cited therein.

21 D. Markovitsi, T.-H. Tran-Thi, R. Even, and J. Simon, *Chem. Phys. Lett.*, **137**, 107 (1987).