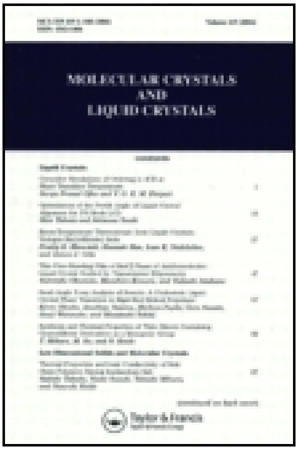

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Discotic Liquid Crystalline Semiconductors

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DISCOTIC LIQUID CRYSTALLINE SEMICONDUCTORS

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Our works on discotic liquid crystalline semiconductors are reviewed. Some of them show very fast carrier mobilities. Novel sandwich rare earth metal complex, bis[octakis(alkylthio)phthalocyaninato]lutetium(III), shows a mobility of 0.71 cm^2*/Vs, which is the fastest in liquid crystals at the present time, so far as we know. It was also found that novel octaphenoxy- and/or hexaphenoxy-substituted phthalocyanine-based discotic liquid crystals exhibit spontaneous perfect homeotropic alignment in the tetragonal columnar mesophase. The corresponding polymer films showing the perfect homeotropic alignment at room temperature could be successfully prepared. Such marvelous films can be practically utilized as organic carrier transport materials and solar batteries.*

Keywords: conductivity; mobility; semiconductor; photoconductor; discotic liquid crystal; phthalocyanine; metallomesogen; homeotropic alignment

1. INTRODUCTION

The participants in this symposium know well that it is past 25 years since the discovery of discotic liquid crystals in 1977. As can be seen from Figure 1, earlier patents of discotic liquid crystals were very few and we did not have any practical applications until 1994. However, an abrupt increase of the number of patents occurred from 1995. This is attributable to an

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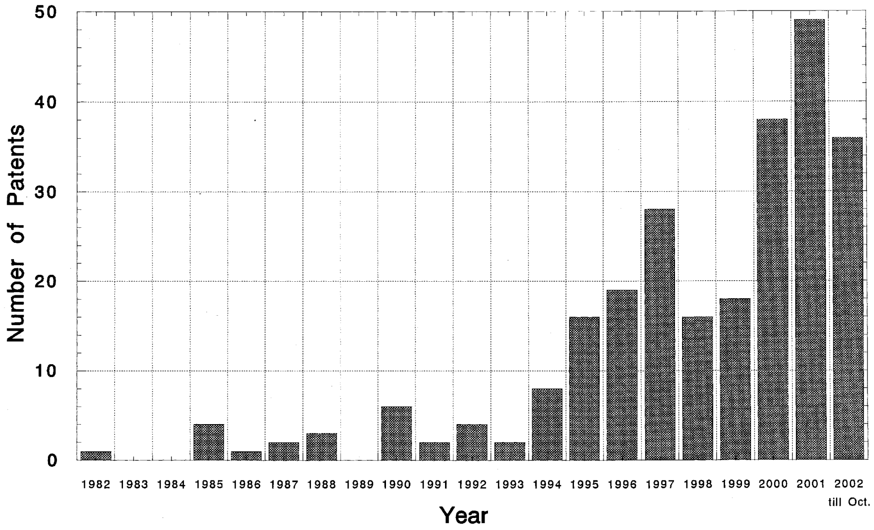


FIGURE 1 Number of patents of discotic liquid crystals per year.

innovation of Wide-view film by Fuji Film Corporation, Kawata and his co-workers. In this symposium, Mr. Kawata will present the innovation.

On the other hand, we are studying discotic liquid crystals for focusing on the following two applications: (1) chromic discotic liquid crystals for direct visualization of intermolecular forces [1]; (2) discotic liquid crystalline semiconductors for carrier transport.

2. A NEW FIELD OF "LIQUID CRYSTALLINE SEMICONDUCTOR"

Recently, a new field which should be called as "liquid crystalline semiconductor" has been opened [2]. Organic carrier transport materials can be practically used in photoreceptors for xerographic copiers and in organic electroluminescent devices. For these applications, the materials are required to have large-area uniformity. For this purpose, the materials are prepared in films either by polymerization or by amorphousization. However, these preparations significantly deteriorate the carrier mobility. For example, molecular single crystals normally show mobilities from 0.1 to 1 cm^2/Vs, but amorphous polymers show the order of $10^{-5} \sim 10^{-6}\,cm^2/Vs$. The order of magnitude decreases by 6. Hence, if liquid crystalline carrier transport materials could be developed, such an undesirable deterioration could be overcome, because liquid crystalline materials show both liquid-like structural flexibility and crystal-like molecular arrangement. These features are favorable for large-area uniformity.

3. HISTORY OF "LIQUID CRYSTALLINE SEMICONDUCTORS"

Hereupon, we look at the brief history of liquid crystalline semiconductors. In 1960's Kusabayashi and Labes already studied photoconductivities of rod-like liquid crystals. However, in the same period, Heilmeyer invented a liquid crystal display, i.e., LCD. Since then, conductivities of liquid crystals have scarcely been studied. In 1977, the first discotic liquid crystal was found by Chandrasekhar et al., and in 1982, Simon and his co-workers pointed out that discotic liquid crystals could be used as one-dimensional conductors. In 1980's, people attempted to synthesize chemically doped discotic liquid crystals to obtain highly conductive, charge transfer complexes, i.e., CT complexes. These CT complexes have, however, a serious problem that they decompose on heating. It is common for organic synthetic chemists that chemical reactions involve transfer of electrons and can be accelerated by heating. Accordingly, the extent of partial electron transfer in CT complexes is largely accelerated at higher temperatures leading to decomposition. Another problem is that the CT complexes formed between π-donor and π-acceptor liquid crystals are insoluble in most of the solvents. Therefore, in 1990's people pursued in measuring high conductivities of non-doped materials, i.e., chemically pure discotic liquid crystals.

4. TOF AND PR-TRMC TECHNIQUES

Irradiation of light on the discotic liquid crystalline materials creates holes and free electrons whose mobilities are measured by means of Time-of-Flight, i.e., TOF, technique. The merits of this technique are as follows. (1) Since the apparatus is relatively small, many groups can undertake the measurements. (2) The electron and hole mobilities can be separately measured. And the demerits being, (1) spontaneous homeotropic alignment is required, which is very hard to obtain especially for discotic liquid crystals. (2) When liquid crystalline materials are packed in the measurement cell, it is necessary to heat the materials over the clearing points. Therefore, a virgin sample cannot be principally measured. As well-known, most of the discotic liquid crystals easily supercool and do not completely come back to the original state.

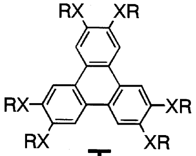
Another method to measure the conductivities and mobilities is Pulse-Radiolysis Time Resolved Microwave Conductivity, abbreviated as PR-TRMC technique [3]. From a huge van de Graaff accelerator, the height of which is equal to about a five storied tower, high velocity of electrons are made to run through a sample to generate holes and free electrons which are the charge carriers. Hence, one can measure the conductivity by this technique. The merits of this technique are as follows. (1) Molecular alignment in the cell is not required. (2) Crystallographically pure, i.e., virgin sample, can be used. Therefore, it is very suitable for discotic liquid crystals. And the demerits being, (1) the apparatus is so huge that very few groups can undertake this technique. Furthermore, (2) the electron and hole mobilities cannot be differentiated.

5. "LIQUID CRYSTALLINE SEMICONDUCTORS" SHOWING HIGH MOBILITIES

Figure 2 lists up the molecular structures of discotic liquid crystalline semiconductors showing very fast mobilities which have recently been found by the above-mentioned techniques. In 1993, Haarer and his coworkers found by using the TOF technique that hexakispentoxytriphenylene, abbreviated as $(C_5O)_6T$ (**1**), shows spontaneous homeotropic alignment in the hexagonal columnar mesophase and exhibits a very fast carrier mobility, 10^{-3} cm^2/Vs [4]. Furthermore, in 1994, they found a much faster carrier mobility, 0.1 cm^2/Vs, in the helical columnar mesophase H of hexakishexylthiotriphenylene, $(C_6S)_6T$ (**2**) [5]. Although these mobilities were interpreted to be due to holes, the origin of the mobility in discotic liquid crystals has not been understood completely. Hence, Yoshino and his coworkers aimed to reveal the origin of positive and negative carrier mobilities of $(C_6O)_6T$ (**3**). Compared with the molecular structures in this figure, a guideline can be extracted to obtain faster mobility-shown in discotic liquid crystals: (1) enlargement of π-system, (2) change from alkoxy to alkylthio group, and (3) synthesis of phthalocyanine sandwich lutetium complex. Hence, we have synthesized many alkoxy-substituted and alkylthio-substituted phthalocyanine derivatives **6** $\sim$ **10**, and found the highest mobility 0.71 cm^2/Vs for the lutetium complex **10**.

6. MEASUREMENTS OF MOBILITIES BY TOF TECHNIQUE FOR THE DISCOTIC LIQUID CRYSTALS BASED ON TRIPHENYLENE

The sample for TOF was prepared as follows: $(C_6O)_6T$ (**3**) was heated over the clearing point and the isotropic liquid was introduced between two ITO glass plates by capillary action. The characteristic feature of the triphenylene-based discotic liquid crystals is to show spontaneous perfect homeotropic alignment without any surface treatments. "Homeotropic



T

1: $(C_5O)_6T$

Col$_h$ $\mu = 10^{-3}$ cm^2/Vs

2: $(C_6S)_6T$

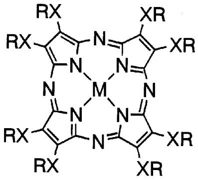
H $\mu = 0.1$ cm^2/Vs

Col$_h$ $\mu = 10^{-3}$ cm^2/Vs

3: $(C_6O)_6T$

Col$_h$ $\mu_{positive} = 10^{-3}$ cm^2/Vs

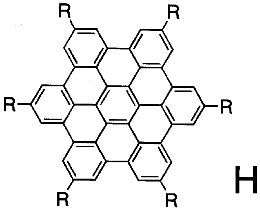
$\mu_{negative} = 10^{-5}$ cm^2/Vs



PM

4: $(C_{10}OC_2)_8PCu$

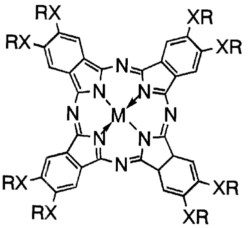
Col 6.5×10^{-2} cm^2/Vs



HBC

5: HBC-C_{12}

Col$_h$ 0.46 cm^2/Vs



PcM

6: $(C_{12}O)_8PcH_2$

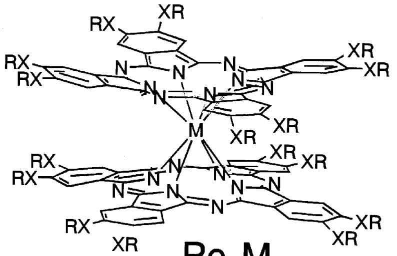
Col$_h$ 5.1×10^{-2} cm^2/Vs

7: $(C_{18}OPh)_8PcH_2$

Col$_h$ 0.25 cm^2/Vs

8: $(C_{12}S)_8PcH_2$

Col$_h$ 0.28 cm^2/Vs



Pc$_2$M

9: $[(C_{12}O)_8Pc]_2Lu$

Col$_h$ 0.17 cm^2/Vs

10: $[(C_{12}S)_8Pc]_2Lu$

Col$_{rh}$ 0.71 cm^2/Vs

Col$_{hh}$ 0.36 cm^2/Vs

FIGURE 2 Molecular structures and mobilities of discotic liquid crystalline semiconductors and photoconductors **1–10**. T: Refs. 4, 5, 6; PM: Ref. 3; HBC-C_{12}: Ref. 16; PcM: Ref. 2; Pc$_2$M: Refs. 10, 11.

alignment" means that, discotic molecules align to form columns perpendicular to the substrate (See Fig. 3). This is the secret of Haarer's success. We have synthesized about 400 discotic liquid crystals in the past 20 years, but we have never encountered such discotics exhibiting spontaneous

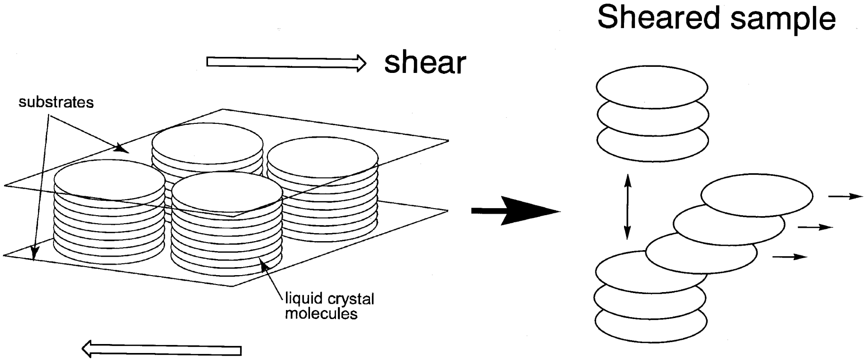


FIGURE 3 The sheared and non-sheared (virgin) sample of $(C_6O)_6T$. See Ref. 6.

homeotropic alignment. The triphenylene derivatives are very exceptional. For these samples, TOF technique has no demerits.

By using TOF technique, Yoshino and his coworkers measured temperature dependence of carrier mobilities for positive and negative carriers in the discotic mesophase of pure and C_{60}-doped $(C_6O)_6T$ [6]. From their precise measurements, it was established that the fast mobility of $(C_6O)_6T$ is originates mainly from the hole mobility.

They also investigated an interesting effect of shearing on the carrier mobilities. Figure 3 illustrates shearing of glass substrates of the measuring cell. It may cause deformation of columnar structure, resulting in decrease of the π-π overlap. In fact, the sheared sample showed slower mobility than the non-sheared sample. Therefore, it is obvious that the perfect homeotropic alignment should be necessary for the TOF measurements.

7. MEASUREMENTS OF MOBILITIES BY PR-TRMC TECHNIQUE FOR THE DISCOTIC LIQUID CRYSTALS BASED ON PHTHALOCYANINE

7.1. Unique Electronic Structure of Pc_2Lu

Next, our phthalocyanine sandwich lutetium complexes (**9** and **10** in Fig. 2) will be described. A series of alkoxy-substituted lutetium complexes $[(C_nO)_8Pc]_2Lu$ (**9**) were synthesized [7]. They vary in the chain length from decyloxy to octadecyloxy. This lutetium complex consists of a Lu^{3+} cation and two Pc^{2-} anions, so that it is not charge-balanced. Hence, the lutetium complex is a neutral radical.

In Figure 4 is shown the MO-diagram of the core Pc_2Lu complex calculated by Aroca and his coworkers [8]. As can be seen from this diagram, a

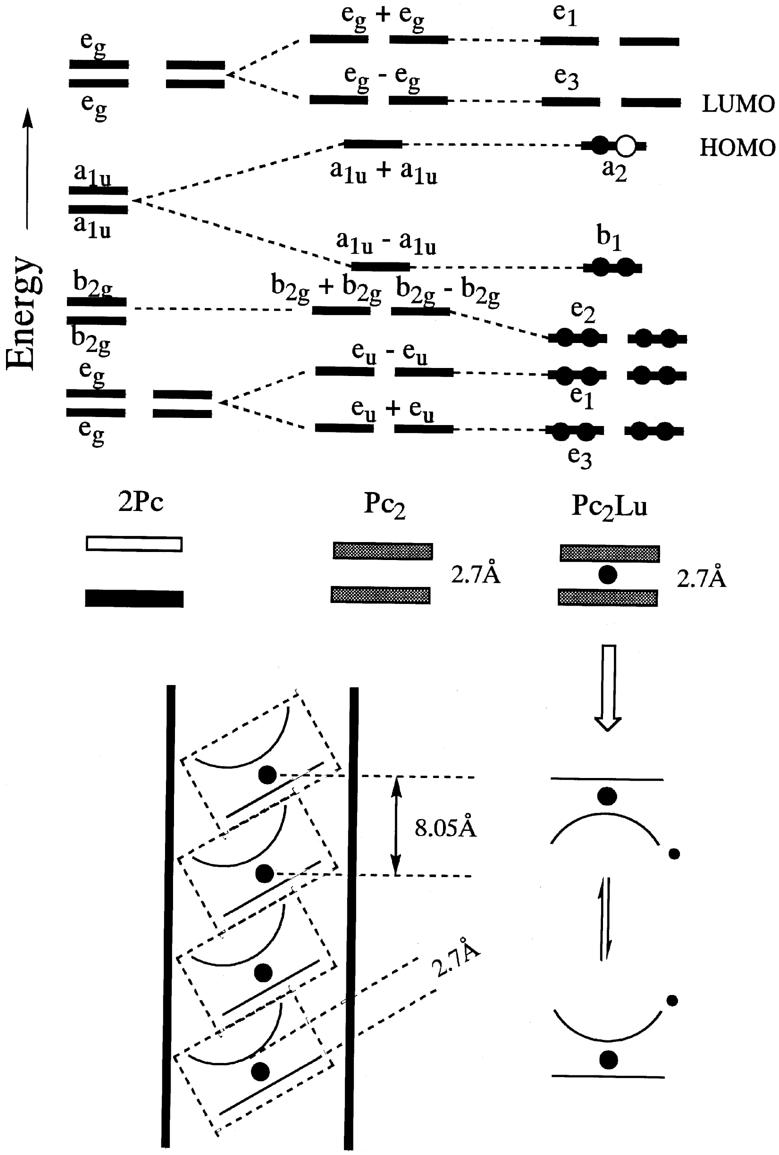


FIGURE 4 Energy diagram of Pc_2Lu calculated by Aroca *et al.*[8] and trampoline movement of the bent phthalocyanine ring by delocalization of a radical electron.

radical electron exists in the HOMO level. In other words, a hole exists in the HOMO level. Since the Pc macrocycle having radical electron lacks the aromaticity, the macrocycle becomes convex. In the crystalline state, the core Pc_2Lu complexes pile up to form columns, as illustrated in this figure. The distance between sandwiches is 8.05 Å. When the long-chain-substituted Pc_2Lu complexes are heated into the liquid crystalline state, the radical electron may go back and forth between two Pc macrocycles. In this case, the Pc macrocycles may move like as trampoline, as shown in this figure.

7.2. $[(C_nO)_8Pc]_2Lu$ Derivatives

Each of the alkoxy-chain-substituted Pc_2Lu complexes $[(C_nO)_8Pc]_2Lu$ (**9**) shows two columnar mesophases. The lower temperature mesophase shows a special phase structure which has not been known so far [7]. As illustrated in Figure 5, the sandwiches pile up at intervals of $2h_t$ in the crystalline state. On the other hand, in the Col_{ho} mesophase only the cofacial stacking distance h_f could be observed. This means that the crystallographic difference between two Pc macrocycles vanishes because of the delocalization of the radical electron. The Col_{ro} intervened between this Col_{ho} and the crystal has a very special columnar structure. In this mesophase, two different stacking distances, h_t and h_f, could be observed at once [7]. Therefore, A and B columns have slipped stacking and cofacial stacking structures, respectively. From the viewpoint of π-π overlap, the π-π overlap enlarges stepwise with changing from crystal to Col_{ho} through Col_{ro}. Hence, the conductivity can be expected to rise stepwise.

As illustrated in the upper part of Figure 6, the conductivities denoted by filled circles actually raised stepwise with increasing temperature [9]. Such a unique behavior has never been reported, so far. On the other hand, the conductivities denoted by open circles show the conductivities on cooling stage from the isotropic liquid (I.L.). These conductivities are much lower than those of the virgin sample on the first heating stage. This means that the discotic compound contained amorphous and supercooled portions for the non-virgin sample. This is a common tendency for most of the discotic liquid crystalline compounds. Discotic compounds do not tend to come back to the original state. We should pay attention to this property.

7.3. $[(C_nS)_8Pc]_2Lu$ Derivatives

Another series of the Pc_2Lu complexes, $[(C_nS)_8Pc]_2Lu$ (**10** in Fig. 2), were synthesized. Judging from the Hammett's σ values, alkoxy group ($\sigma_p = -0.27$) is an electro-donating group, whereas alkylthio group ($\sigma_p = 0$) is neither electro-donating nor electro-withdrawing group. Hence, we expected that if the phthalocyanine lutetium complex would be substituted by alkylthio groups, the band gap between HOMO and LUMO would become smaller. This may lead to higher electroconductivity. Hence, we

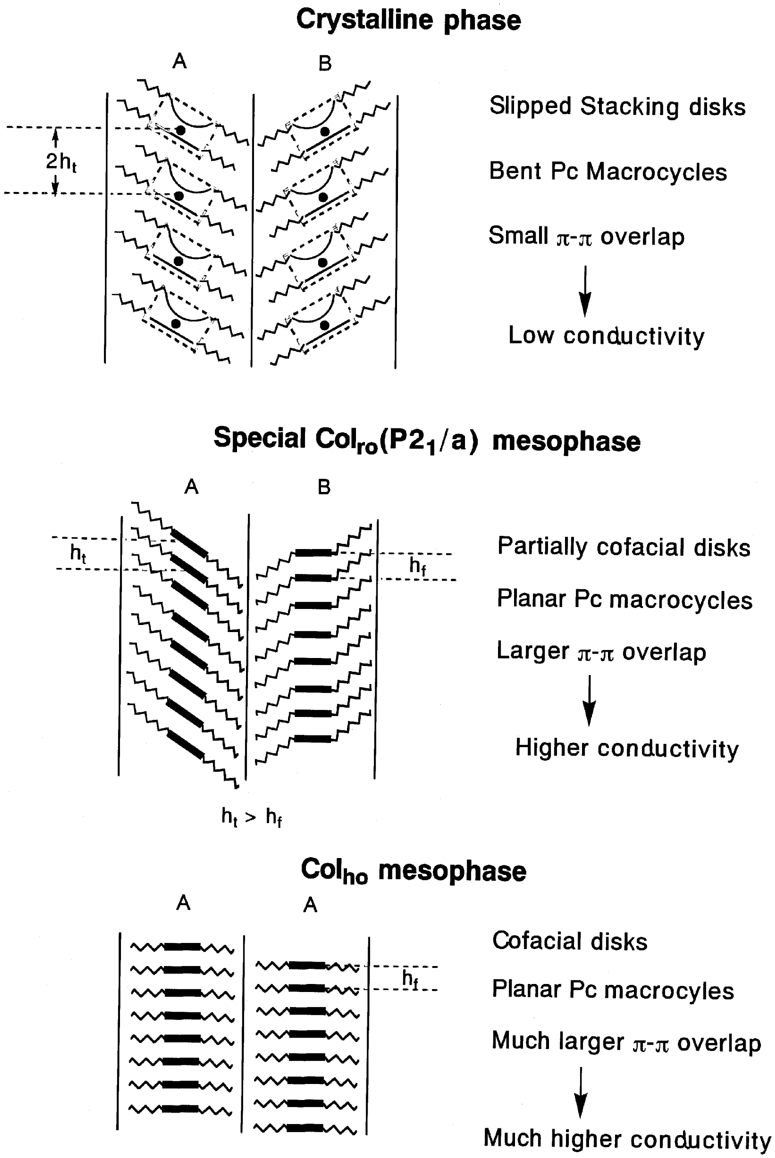
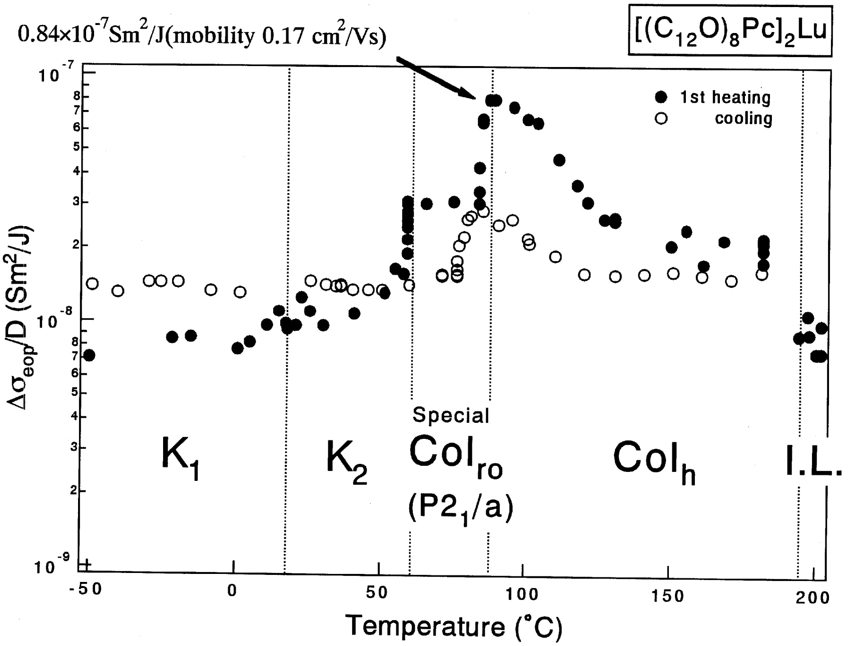


FIGURE 5 Stepwise enlargement of π-π overlap in the various columnar structures in the $[(C_nO)_8Pc]_2Lu$ (**9**) complex.

have synthesized novel alkylthio-substituted phthalocyanines, bis[octakis(alkylthio)phthaocyaninato]lutetium(III), europium(III), terbium(IIII), (abbreviated as $[(C_nS)_8Pc]_2M$: M = Lu, Eu, Tb), and investigated their



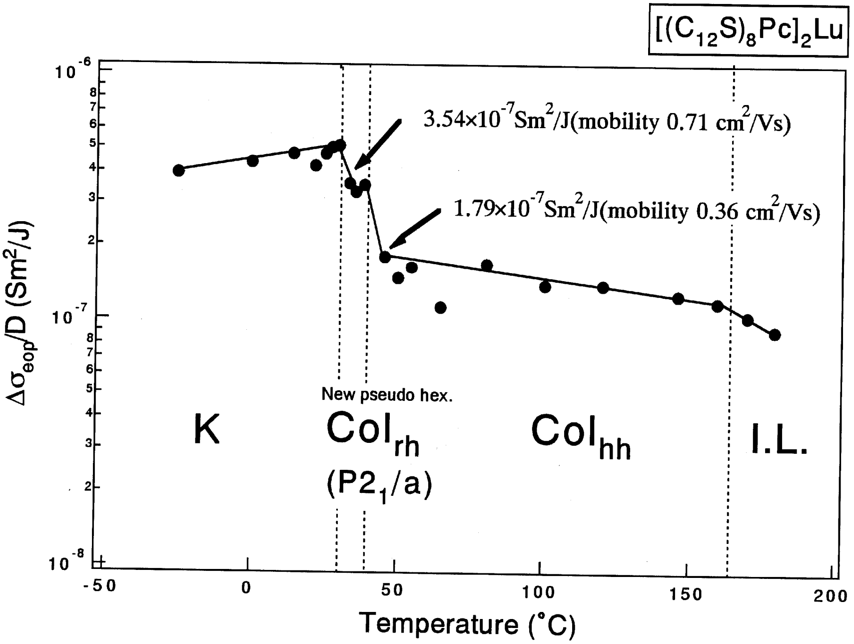


FIGURE 6 Conductivities versus temperatures for the $[(C_{12}O)_8Pc]_2Lu$ (**9**) and $[(C_{12}S)_8Pc]_2Lu$ (**10**) derivatives.

mesomorphism and conductivities [10]. Each of the rare metal complexes shows very similar phase transitions, and has a hexagonal columnar mesophase, Col_h. For n = 10,12,14, they show a new unknown mesophase M at around room temperature.

From the detailed X-ray structural analysis, this lower-temperature mesophase M was established as a novel pseudo hexagonal columnar mesophase. A model fitting for this novel pseudo hexagonal columnar mesophase is shown in Figure 7(3), together with another pseudo Col_{ho} mesophase [Fig. 7(1)] which was previously found by Skoulios *et al.* [11]. In the present pseudo Col_{ho} mesophase [Fig. 7(3)], the central Pc cores regularly stack face-to-face at intervals of ca. 3.3 Å and packed in a 2D-hexagonal lattice, whereas the whole molecules are packed in a rectangular lattice [10]. On the other hand, in the previous pseudo Col_{ho} mesophase [Fig. 7(1)], the cores are packed in rectangular lattice and the whole molecules are packed in a 2D-hexagonal lattice [11]. It is quite opposite to the present pseudo Col_{ho} mesophase. Also this phase is different from the previous special Col_{ro} mesophase [7] [Fig. 7(2)] of $[(C_nO)_8Pc]_2Lu$ (**9**).

In the lower part of Figure 6, electroconductivities of $[(C_{12}S)_8Pc]_2Lu$ (**10**) are plotted against temperatures. The conductivity of this alkylthio-substituted one decreases at these phase transitions. However, all the conductivities in these mesophases show higher than the top value of the previous alkoxy-substituted derivative, $[(C_{12}O)_8Pc]_2Lu$ (**9**). Furthermore, the mobility, 0.71 cm^2/Vs, of the novel pseudo Col_{ho} mesophase is the fastest in liquid crystals at the present time, so far as we know [10]. This value is comparable to the mobility, 1 cm^2/Vs, of amorphous silicon which is now employed for practical usage.

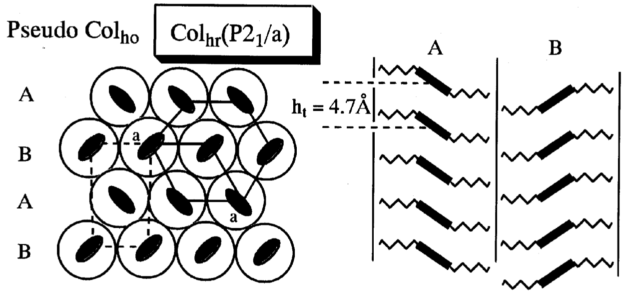
Thus, in order to obtain better liquid crystalline semiconductors, the following three points are very useful: (1) synthesis of phthalocyanine sandwich lutetium complexes, (2) enlargement of the π-system, and (3) substitution by alkylthio group. If they will be then used for the practical applications as organic carrier transport materials, (4) large-area uniformity and (5) large-area film formation should be required.

8. PC-BASED DISCOTIC LIQUID CRYSTALS SHOWING PERFECT SPONTANEOUS HOMEOTROPIC ALIGNMENT

8.1. Materials Showing Homeotropic Alignment at High Temperatures

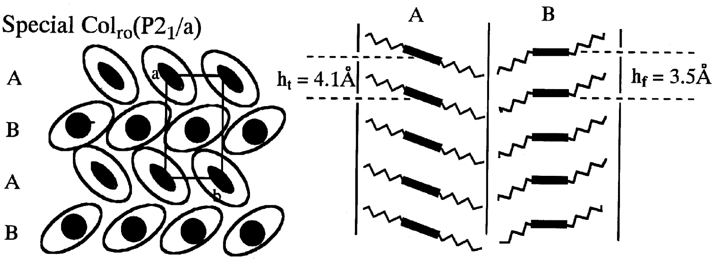
Generally, discotic liquid crystals are so viscous that polydomains and defects often arise. Both polydomain and defects suppress the carrier transport. Recently, we succeeded to synthesize a novel type of octaphenoxy-substituted phthalocyaninato copper complexes (**13** in Scheme 1),

(1) Conventional pseudohexagonal mesophase: **Ref.[11].**



Symmetry { Whole molecules : 2D-hexagonal
Cores : 2D-rectangular $P2_1/a = P2_12_1$

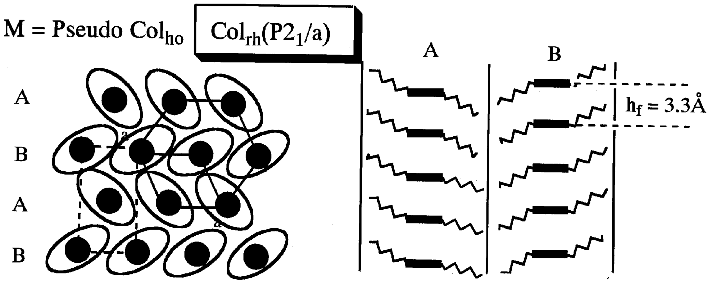
(2) New type of Col$_{ro}$(P2$_1$/a) mesophase: **Ref.[7].**



Symmetry: 2D-rectangular $P2_1/a$

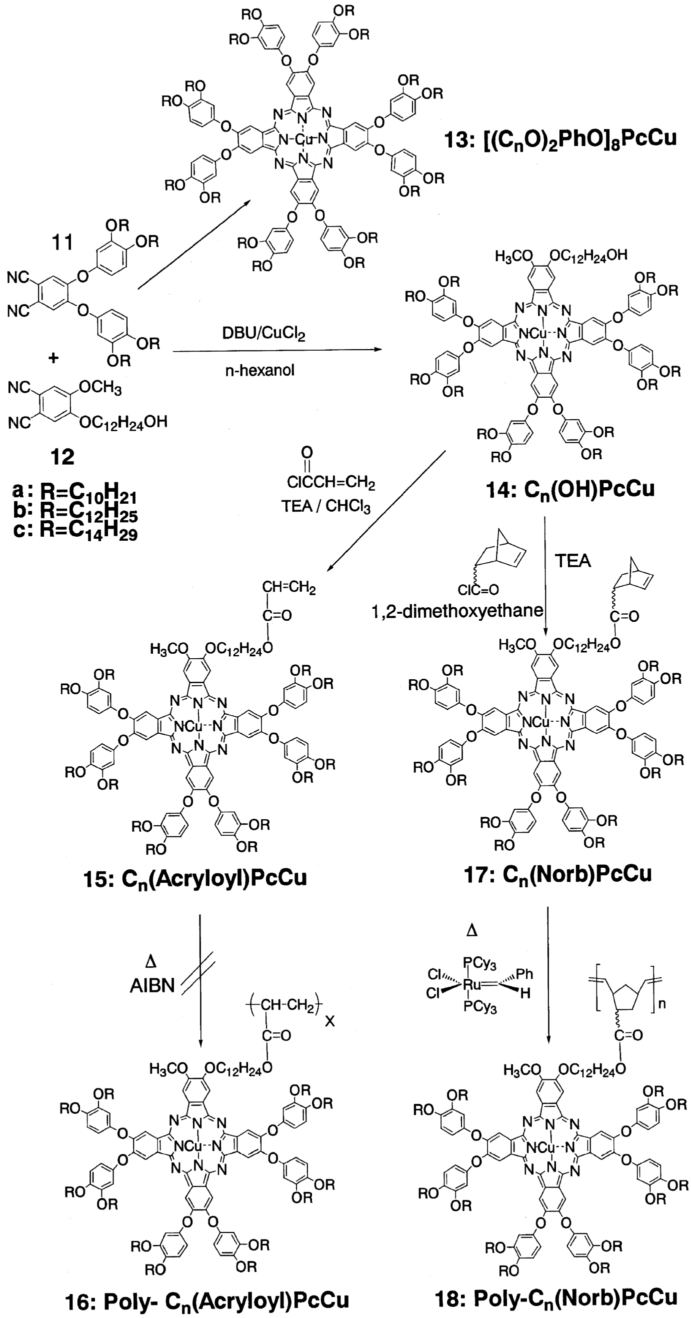
Hence, two different stacking distances, h_t and h_f, can be observed for X-ray.

(3) Novel pseudohexagonal mesophase: **Ref.[10].**



Symmetry { Whole molecules : 2D-rectangular($P2_1/a$)
Cores : 2D-hexagonal

FIGURE 7 Novel pseudohexagonal mesophase and the related mesophases.



SCHEME 1 Synththic route of phthalocyanine derivatives **14–18** DBU = 1,8-diazabicyclo[5,4,0]-7-undecene, TEA = triethylamine and AIBN = α, α-azobisisobuthyronitrile.

and found they show spontaneous monodomain homeotropic alignment for the tetragonal columnar mesophase between two glass plates without any surface treatments [12].

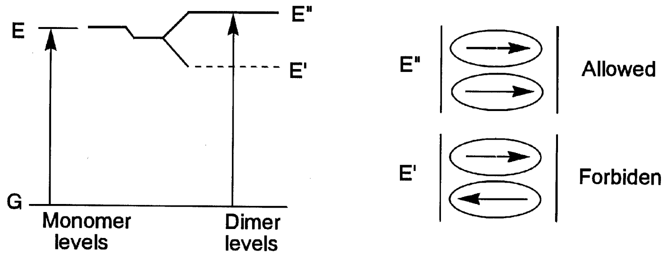
A series of the phthalocyanine derivatives (**13**) having different length of alkoxy chains show quite rich mesophases; $\mathrm{Col_h}$, $\mathrm{Col_r}1$, $\mathrm{Col_r}2$, $\mathrm{Col_r}3$, $\mathrm{Col_{tet}}$ and Cub, although the lowest temperature phase X could not be identified. Very interestingly, the $\mathrm{Col_h}$ mesophase having higher symmetry exists at the lower temperatures, whereas the $\mathrm{Col_r}$ mesophase having lower symmetry exists at the higher temperatures. It is quite opposite to the general tendency. There are three different $\mathrm{Col_r}$ mesophases having the same symmetry $P2_1/a$. This is originated from different stacking structures. This problem was considered from the temperature-dependent electronic spectra of the thin film.

According to Kasha's rule [13], the electronic spectra are affected by interaction between two neighboring molecules in various dimers (Fig. 8). The cofacial dimers, in-line dimers, and slipped stacking dimers show no split of the related band (in the case of phthalocyanines, it corresponds to the Q-band which is a big absorption band normally appears at 600–800 nm). Only the oblique dimers show the Q-band splitting. In-line dimers can be automatically excluded, because such a dimer cannot form in any columnar mesophases. The temperature-dependent electronic spectra of a film of the representative derivative $[(C_{12}O)_2PhO]_8PcCu$ (**13b**) are shown in Figure 9[A]. As can be seen from this figure, the X phase at room temperature gave split Q-bands at about 610 nm and 750 nm. On the other hand, the almost single Q-band could be observed at about 630 nm for the higher temperature mesophases, $\mathrm{Col_r}2$, $\mathrm{Col_{tet}}$ and Cub. The intermediate temperature mesophases, $\mathrm{Col_h}$ and $\mathrm{Col_r}1$, gave intermediate spectra. They can be formed by superimposition of the curves of the higher and lower temperature mesophases.

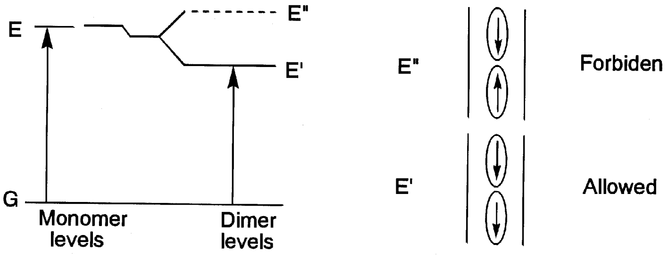
Taking account of both results of the temperature-dependent electronic spectra and the X-ray diffraction studies, the stacking structures in columns are depicted in Figure 10. In the X phase, the molecules form roof-top-shaped dimers (Fig. 10[C]). On heating these dimers begin to freely rotate to show precession movement in the intermediate mesophases. The roof-top-shaped dimers may be partially destroyed by the precession movement, so that equilibrium between the roof-top-shaped dimers and rotating monomers may coexist. For this case, two different stacking distances can coexist at h_1 and h_2 (Fig. 10[B]). On further heating, the roof-top-shaped dimers are totally destroyed into the coplanar or cofacial monomers in the higher temperature mesophases (Fig. 10[A]).

Uniform monodomain homeotropic alignment could be achieved for the $\mathrm{Col_{tet}}$ mesophase between two soda-lime or quartz glass plates [12]. The glass surfaces were not treated by any surfactants. There were neither

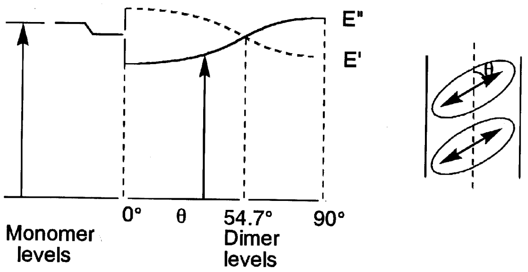
(a) Parallel(cofacial) transition dipoles: Blue-shift case



(b) In-line transition dipoles: Red-shift case



(c) Co-planar(slipped) transition dipoles: Shift depends on angle θ.



(d) Oblique(herringbone) transition dipoles: Band-splitting case

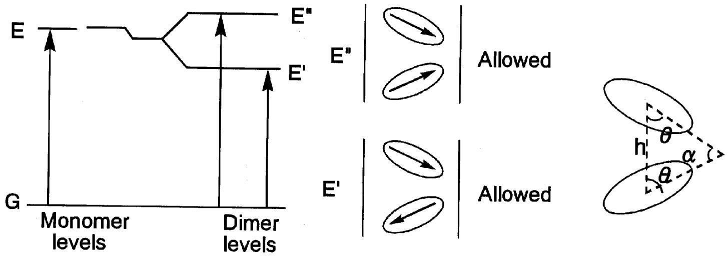


FIGURE 8 Exciton energy diagrams for various dimers. See Ref. 13.

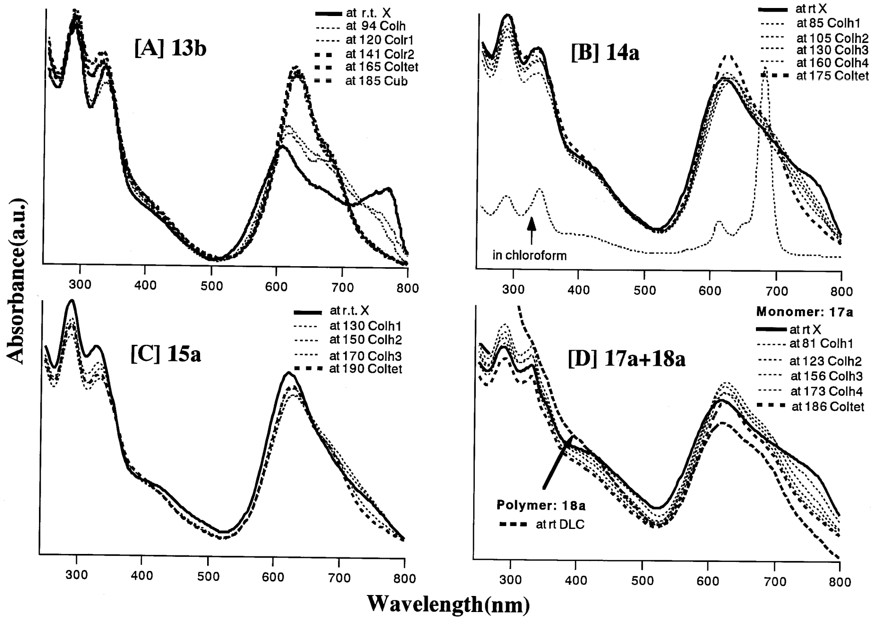


FIGURE 9 Temperature-dependent electronic spectra in UV-Vis region of the casting films: [A] $[(C_{12}O)_2PhO]_8PcCu$: **13b**; [B] $C_{10}(OH)PcCu$: **14a**; [C] C_{10}(Acryloyl)PcCu: **15a**; [D] C_{10}(Norb)PcCu: **17a** and poly-C_{10}(Norb)PcCu: **18a**.

polydomains nor disclinations. Although this reason is not clear at the present time, we think as follows. The lone pairs of oxygen atoms in the phenoxy groups of this copper complex (**13** in Scheme 1) may coordinate to the dangling bonds of silicon atoms on the surface of glass. The first Pc disk adhered to the surface may trigger the stacking of the disks one after another to make columns normal to the surface. This model was speculated from water adhesion to glass surface. Further studies should be necessary.

Our next targets are to obtain the film showing homeotropic alignment at room temperature and to fix the spontaneous homeotropic alignment of the Col_{tet} mesophase by polymerization. If such a film can be prepared by using our phthalocyanine derivatives (**13**), it will be very useful for practical applications.

8.2. Fixation of the Homeotropic Alignment by Polymerization

According to Scheme 1, we introduced a polymerizable group into the compound, remaining the property of spontaneous homeotropic alignment in the Col_{tet} phase. At first, the dicyano derivatives, **11** and **12**, were

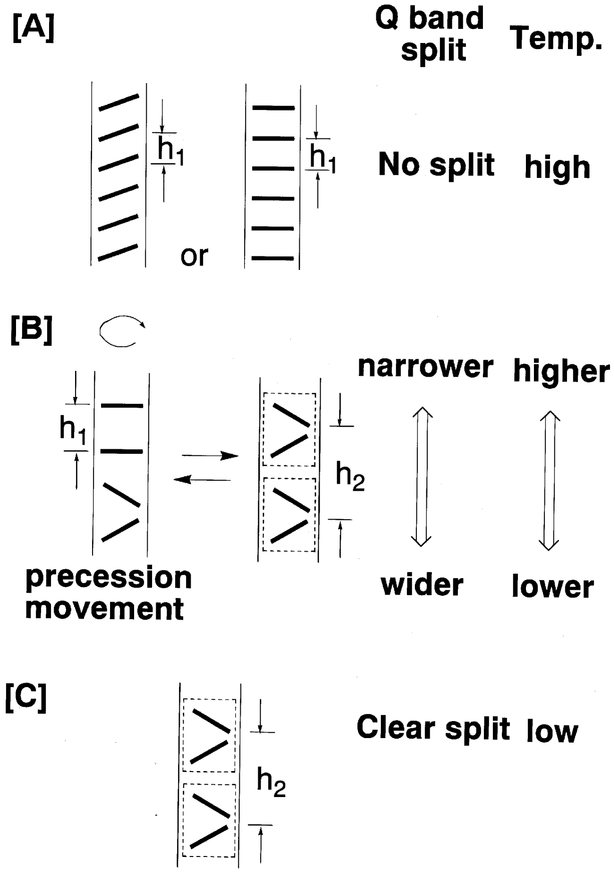
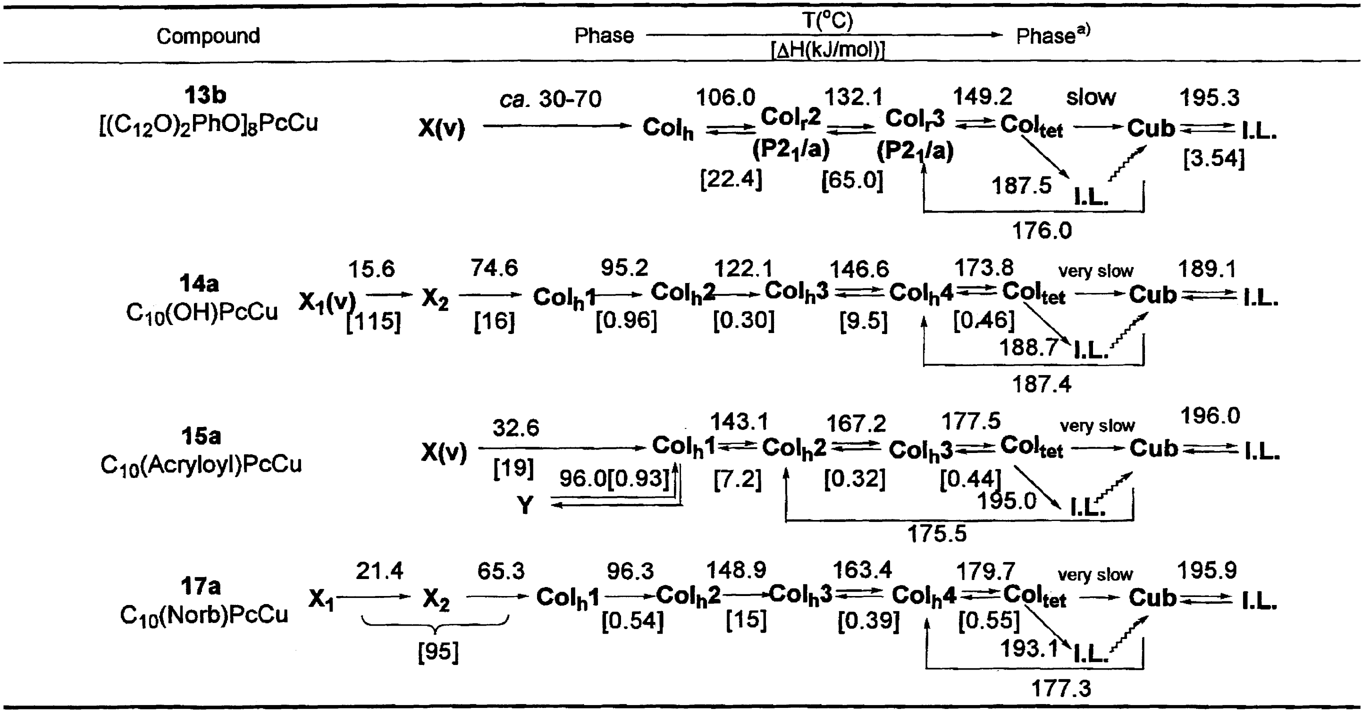


FIGURE 10 Relationship of the stacking structure in column to the Q band split and temperature.

mingled in a ratio of 1:3 to synthesize the compound **14** having a hydroxy group at the terminal end of one long chain, and having six phenoxy groups. The previous compounds **13** show perfect spontaneous homeotropic alignment, which may be due to the eight phenoxy groups. Therefore, much less number of the phenoxy groups might lead to non-homeotropic alignment, so that the number six might be good for the new compound, **14**. Compound **14** was further converted into compounds, **15** and **17**, substituted by polymerizable groups, acryloyl and norbornene, respectively.

When the chain length (n) is ten ($n = 10$), the compounds **14a**, **15a** and **17a** show the phase transitions as summarized in Table 1. As can be seen

TABLE 1 Phase Transition Temperatures and Enthalpy Changes of the Phthalocyanine Derivatives, $[(C_{12}O)_2PhO]_8PcCu$: **13b**, $C_{10}(OH)PcCu$: **14a**, C_{10} (Acryloyl)PcCu: **15a** and C_{10}(Norb)PcCu: **17a**



Compound	Phase $\xrightarrow[{[\Delta H(kJ/mol)]}]{T(^{\circ}C)}$ Phase[a)]
13b $[(C_{12}O)_2PhO]_8PcCu$	$X(v) \xrightarrow{ca.\ 30\text{-}70} Col_h \xrightleftharpoons[{[22.4]}]{106.0} \underset{(P2_1/a)}{Col_r2} \xrightleftharpoons[{[65.0]}]{132.1} \underset{(P2_1/a)}{Col_r3} \xrightleftharpoons{149.2} Col_{tet} \xrightarrow{slow} Cub \xrightleftharpoons[{[3.54]}]{195.3} I.L.$ $Col_{tet} \xrightarrow{187.5} I.L. \rightsquigarrow Cub$ $I.L. \xrightarrow{176.0} Col_r3$
14a $C_{10}(OH)PcCu$	$X_1(v) \xrightarrow[{[115]}]{15.6} X_2 \xrightarrow[{[16]}]{74.6} Col_h1 \xrightarrow[{[0.96]}]{95.2} Col_h2 \xrightarrow[{[0.30]}]{122.1} Col_h3 \xrightleftharpoons[{[9.5]}]{146.6} Col_h4 \xrightleftharpoons[{[0.46]}]{173.8} Col_{tet} \xrightarrow{very\ slow} Cub \xrightleftharpoons{189.1} I.L.$ $Col_{tet} \xrightarrow{188.7} I.L. \rightsquigarrow Cub$ $I.L. \xrightarrow{187.4} Col_h4$
15a C_{10}(Acryloyl)PcCu	$X(v) \xrightarrow[{[19]}]{32.6} Col_h1 \xrightleftharpoons[{[7.2]}]{143.1} Col_h2 \xrightleftharpoons[{[0.32]}]{167.2} Col_h3 \xrightleftharpoons[{[0.44]}]{177.5} Col_{tet} \xrightarrow{very\ slow} Cub \xrightleftharpoons{196.0} I.L.$ $Col_h1 \xrightarrow{96.0[0.93]} Y$ $Col_{tet} \xrightarrow{195.0} I.L. \rightsquigarrow Cub$ $I.L. \xrightarrow{175.5} Col_h2$
17a C_{10}(Norb)PcCu	$X_1 \xrightarrow{21.4} X_2 \xrightarrow{65.3} Col_h1$ $\underbrace{\qquad}_{[95]}$ $Col_h1 \xrightarrow[{[0.54]}]{96.3} Col_h2 \xrightarrow[{[15]}]{148.9} Col_h3 \xrightleftharpoons[{[0.39]}]{163.4} Col_h4 \xrightleftharpoons[{[0.55]}]{179.7} Col_{tet} \xrightarrow{very\ slow} Cub \xrightleftharpoons{195.9} I.L.$ $Col_{tet} \xrightarrow{193.1} I.L. \rightsquigarrow Cub$ $I.L. \xrightarrow{177.3} Col_h4$

[a)] Phase nomenclature: Col_h = hexagonal columnar mesophase, Col_r = rectangularl columnar mesophase, Col_{tet} = tetragonal columnar mesophase, X and Y = unidentified mesophases, Cub = cubic phase and I.L. = isotropic liquid. All heating and cooling rates for the DSC measurements were 2.5°C/min. All the Col_{tet} mesophases shown perfect homeotropic alignment.

from this table, these compounds **14a**, **15a** and **17a** show almost the same phase transition behavior. They show unidentified mesophases X and Y in the lower temperature region, plural $\mathrm{Col_h}$ mesophases in the medium temperature region, and $\mathrm{Col_{tet}}$ and Cub mesophases in the higher temperature region. These behaviors are very similar to the previous octaphenoxy-group-substituted compound **13b**. Compounds, **14**, **15** and **17**, exhibit perfect spontaneous homeotropic alignment in the $\mathrm{Col_{tet}}$ mesophase, according to our expectation. As can be seen from Figure 9[B], [C] and [D], the spectra of the thin films of **14a**, **15a** and **17a** gave a non-splitting Q-band for all the $\mathrm{Col_{tet}}$ mesophases at high temperatures. Therefore, the disks pile up face-to-face in these $\mathrm{Col_{tet}}$ mesophases. As can be seen from this figure [B] and [D], a weak Q-band splitting could be detected for the X phase of **14a** and **17a** at room temperature. As can be seen from this figure [C], the acryloyl derivative **15a** gave an almost non-splitting Q-band for the X phase at room temperature. This means that the derivative **15a** shows almost nearly face-to-face stacking even at room temperature.

Next, this homeotropic alignment of the monomers was served for the fixation by polymerization. A chloroform solution containing the monomer and catalyst was cast onto a glass plate to form the thin film. The film on the glass plate was set in a Mettler hot stage, heated at 185°C for two hours, and then cooled to room temperature. Degrees of polymerization were checked by MALDI-TOF mass spectra. The acryloyl derivative **15** little polymerized

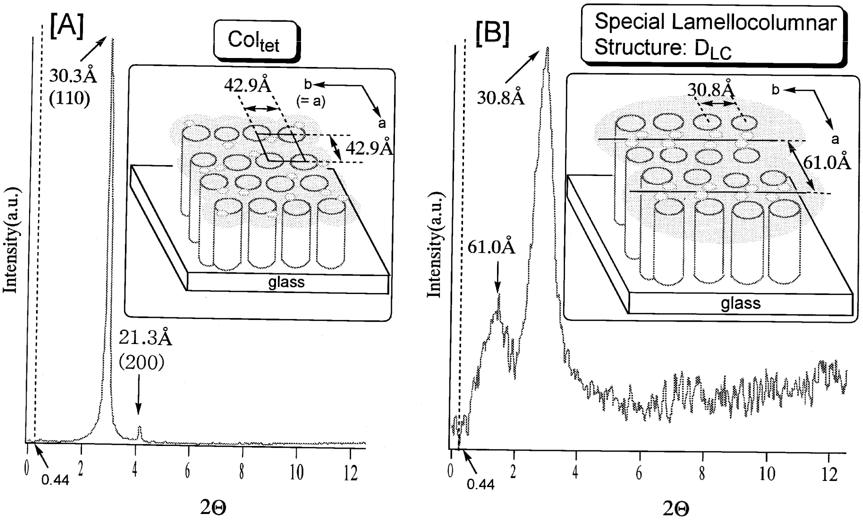


FIGURE 11 Small angle X-ray diffraction patterns of [A]: $\mathrm{C_{10}}$(Norb)PcCu **6a** at 185°C and [B]: poly-$\mathrm{C_{10}}$(Norb)PcCu **7a** at room temperature.

and merely showed unreacted monomer and a small amount of multimers; tetramer at most [14]. On the other hand, the norbornene derivative **17** was well polymerized [15]. Accordingly, the ring-opening metathesis polymerization by using Grubbs catalyst is very suitable for the polymerization of this system. As can be seen from Figure 9[D], the spectrum of polymer **18a** at room temperature gave the same spectrum of monomer **17a** in $\mathrm{Col_{tet}}$ mesophase at 185°C. This implies that the face-to-face stacking at the high temperature could be successfully fixed at room temperature.

Figure 11 shows small angle X-ray diffraction patterns of the monomer **14a** and the corresponding polymer **17a**. The monomer **17a** at 185°C gave two sharp reflections at 30.3 Å and 21.3 Å, which ratio is $1/\sqrt{2}:1/2$. This ratio means that the mesophase is a $\mathrm{Col_{tet}}$ phase. The mesophase structure is illustrated in the left inset in this figure. On the other hand, the polymer **18a** at room temperature gave two reflections at 61.0 Å and 30.8 Å, which ratio is 1:1/2. This means that the phase shows a lamellar structure. The reflection at 61.0 Å appears only for the polymer. Thereby, the monomers polymerized in a fastener-like fashion, and the facing columns may form layers; the layer distance may correspond to 61.0 Å, as illustrated in the right inset in this figure. If it would be a conventional lamellar structure, the first order reflection at 61.0 Å should be much stronger than the second order reflection at 30.8 Å. However, for the present lamellar mesophase the intensity of the reflection at 61.0 Å is much weaker than that of the reflection at 30.8 Å. It is very extraordinary. The reflection at 30.8 Å may be due to the spacing between the neighboring molecules in the b-axis direction, as illustrated in this inset. The value $b = 30.8$ Å is significantly shorter than the value $b = 42.9$ Å for the monomer. Accordingly, the molecules may considerably interdigitate into each other. Hence, we propose a special lamellocolumnar structure for the polymer, as illustrated in this inset [15].

9. CONCLUSION

Thus, this marvelous property of spontaneous homeotropic alignment in the $\mathrm{Col_{tet}}$ mesophase enables us to easily prepare the large-area uniform film. Since fast carrier mobility can be expected for the present phthalocyanine-based discotic liquid crystals, they can be applied in an organic electroluminescent device as the carrier transport layer and also solar batteries.

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