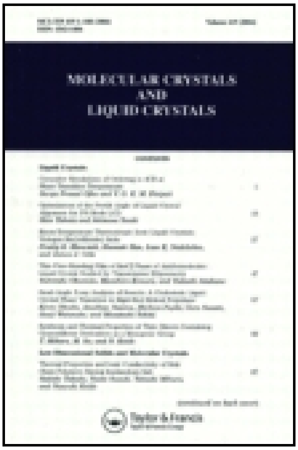


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Discotic Liquid Crystals of Transition Metal Complexes, 4:[1] Novel Discotic Liquid Crystals Obtained from Substituted Bis(dithiolene)nickel Complexes by a New Method

Kazuchika Ohta [a], Akira Takagi [a], Hiromitsu Muroki [a], Iwao Yamamoto [a], Kei Matsuzaki [a], Tamotsu Inabe [b] & Yusei Maruyama [b]

[a] Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386, Japan

[b] Department of Molecular Assemblies, Institute for Molecular Science, Okazaki, 444, Japan

Version of record first published: 28 Mar 2007.

To cite this article: Kazuchika Ohta, Akira Takagi, Hiromitsu Muroki, Iwao Yamamoto, Kei Matsuzaki, Tamotsu Inabe & Yusei Maruyama (1987): Discotic Liquid Crystals of Transition Metal Complexes, 4:[1] Novel Discotic Liquid Crystals Obtained from Substituted Bis(dithiolene)nickel Complexes by a New Method, Molecular Crystals and Liquid Crystals, 147:1, 15-24

To link to this article: http://dx.doi.org/10.1080/00268948708084621

Mol. Cryst. Liq. Cryst., 1987, Vol. 147, pp. 15–24
Photocopying permitted by license only

Printed in the United States of America

Discotic Liquid Crystals of Transition Metal Complexes, 4:[1] Novel Discotic Liquid Crystals Obtained from Substituted Bis(dithiolene)nickel Complexes by a New Method

KAZUCHIKA OHTA, AKIRA TAKAGI, HIROMITSU MUROKI, IWAO YAMAMOTO, and KEI MATSUZAKI

Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386 Japan

and

TAMOTSU INABE and YUSEI MARUYAMA

Department of Molecular Assemblies, Institute for Molecular Science, Okazaki, 444 Japan

(*Received July 15, 1986; in final form September 1, 1986*)

Two new disc-like complexes, bis[1,2-di(p-nonyloxyphenyl)ethane-1,2-dithiolene]nickel (6a) and bis[1,2-di-(p-undecyloxyphenyl)ethane-1,2-dithiolene]nickel (6b), have been synthesized by a new method. It was found that the complexes exhibit discotic mesomorphism. The half-wave potentials for the reduction of the nickel complexes (6a, b) determined by cyclic voltammetry, are -0.06V (6a) and -0.07V for (6b) vs. SCE in CH_2Cl_2. The nickel complexes (6a,b) are only a few examples of π-acceptor discotic liquid crystals.

Keywords: discotic liquid crystal, transition metal complex, bis(dithiolene)nickel, π-acceptor, one-dimensional organic conductor

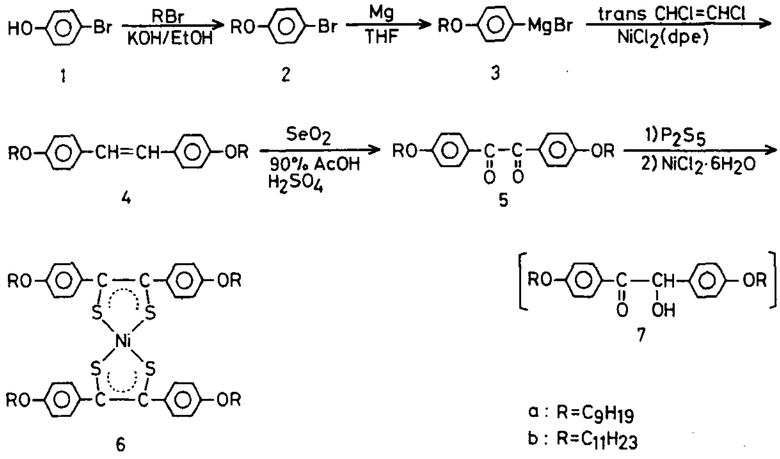
INTRODUCTION

Discotic liquid crystals[2] have potential as one-dimensional organic conductors, because they readily construct a columnar structure essential to organic conductors.[3] Most of the molecules exhibiting discotic mesophases consist of a flat core in the center with several long alkyl chains in the surroundings.[4] Introduction of the long alkyl chains to the flat molecule generates two interesting properties: (1) the distance of the parallel stacking of these molecules decrease in the columnar structure, and (2) the molten alkyl chains surrounding the columns create an apolar medium that permits the dissolution of various organic dopants without disrupting the conducting chains.[5] These properties have a good effect on obtaining one-dimensional organic conductors. There have been reports of charge transfer complexes formed between π-donor discotic liquid crystals and tetracyanoquinodimethane etc.[5,6] However, only one "disc-like π-acceptor" which exhibits mesomorphism has been synthesized.[7] In focusing our interest on the preparation of a novel π-acceptor exhibiting discotic mesomorphism, two new disc-like complexes, bis[1,2-di(p-n-nonyloxyphenyl)ethane-1,2-dithione]nickel (6a) and bis[1,2-di(p-n-undecyloxyphenyl)ethane-1,2-dithione]nickel (6b), have been synthesized by a new method. It was found that the complexes exhibit discotic mesomorphism. These are only a few examples of π-acceptor discotic liquid crystals. So, we wish to report here the synthesis and properties of the complexes (6a,b).

RESULTS AND DISCUSSION

Synthesis

Synthesis of the present nickel complexes were carried out using the method illustrated in Scheme 1. The unsubstituted complex, bis(1,2-diphenylethane-1,2-dithione)nickel, has been prepared from benzoin in 35% yield, by the method reported by Schrauzer *et al.*[8] We found that the substituted benzoin (7a,b) cannot be synthesized from p-n-alkoxybenzaldehyde by benzoin condensation, but that the substituted benzils (5a,b) can be transformed into the desired target complexes (6a,b) in 57% (6a) and 59% yield (6b), respectively. The substituted benzils (5a,b) were synthesized from the substituted stilbenes (4a,b) in 33% (5a) and 28% yield (5b) respectively, by a modification of Sonoda's method. Unsubstituted benzil was obtained from stilbene in 86% yield, although Sonoda *et al.* reported that benzil can be selectively synthesized from diphenylacetylene in 84% yield.[9] The substituted stilbenes (4a,b) could be easily prepared from the corresponding p-n-alkoxybromobenzenes (2a,b) in relatively good yield; 49% for cis- and trans-isomers of (4a) and 61% for cis- and trans-



Scheme 1 Synthetic scheme for the long chains substituted bis(dithiolene)nickel complexes (6a,b).

isomers of (4b), using the method reported by Tamao *et al.*[10] Although the Wittig reaction is conventionally used for the preparation of stilbenes,[11,12] this method was very tedious and the yield of the substituted stilbenes was low (24%,[11] 27%[12]).

Discotic mesomorphism

It was found that the complexes, (6a) and (6b), exhibit discotic mesomorphism. The phase transitions for the complexes are summarized in Table I. The K_2 crystals of (6a) could be obtained as black needle-like crystals only by recrystallization from ethyl acetate. The K_2 crystal could not be obtained by any thermal treatment. When the isotropic liquid of (6a), which has a clearing point 189°C, was cooled down to room temperature, it turned into another crystalline phase K_1 (plate-like) via the *D* phase. The same behavior was observed for (6b). However, recrystallization of (6b) from ethyl acetate always gave a mixture of K_2 (needle-like) crystals and K_1 (plate-like) crystals (small amount). So, we were unable to determine the enthalpy change (ΔH_t) of the phase transition at 118°C.

The phase between 109 and 189°C of (6a) and the phase between 88 and 177°C of (6b) were established as discotic mesophases by miscibility tests using a differential scanning calorimeter and by observation of the phases using a polarizing microscope. Through constructing the binary phase diagram between (6a) and (6b) (Figure 1) by the miscibility test, it was found that the *D* phase of (6a) is totally

TABLE I

Transition temperatures (T_t) and enthalpy changes (ΔH_t) of the nickel complexes, 6a and 6b

Compound	Phase[a] $\xrightarrow[\Delta H_t(\text{kcal/mol})]{T_t(^\circ\text{C})}$ Phase
6a	$K_2 \xrightarrow[8.1]{130} D$ $K_1 \xrightarrow[6.2]{109} D \xrightarrow[15.3]{189} \text{I.L.}$
6b	$K_2 \xrightarrow{118} D$ $K_1 \xrightarrow[7.6]{88} D \xrightarrow[14.5]{177} \text{I.L.}$

[a] Phase nomenclatures: K = crystal, D = discotic liquid crystal, I.L. = isotropic liquid.

miscible in the *D* phase of (6b), and that a eutectic point exists at 52 wt% of (6a) at 40°C. If the *D* phases of (6a) and (6b) were not discotic mesophases but crystals, such a eutectic point could not be observed. Both of the *D* phases gave a plane texture surrounded by a lustrous ring (Figure 2) which resembled well the texture of the discotic mesophase D_1 in C_8-Cu(II) reported previously.[13] For the reasons mentioned above, therefore, it was concluded that the *D* phases of (6a) and (6b) are both discotic mesophases. These are only a few examples of the nickel complexes exhibiting discotic mesomorphism in transition metal complexes.[7,14]

Electrochemistry

The half-wave potentials for the reduction, $E_{1/2}$, of the series ($NiS_4C_4H_4$, $NiS_4C_4(n\text{-}C_8H_{17})_4$, $NiS_4C_4Ph_4$, $NiS_4C_4(p\text{-}n\text{-}C_9H_{19}O\text{-}Ph)_4$, $NiS_4C_4(p\text{-}n\text{-}C_{11}H_{23}O\text{-}Ph)_4$) are given in Table II. It is obvious from this table that the complex substituted by phenyl groups, $NiS_4C_4Ph_4$, becomes a much better acceptor than the complex substituted by octyl groups, $NiS_4C_4(n\text{-}C_8H_{17})_4$. The complex does not have a discotic mesophase but exhibits a single melting into isotropic liquid at 49°C, although the $NiS_4C_4(n\text{-}C_8H_{17})_4$ complex has the long alkyl chains. On the other hand, the complexes substituted by long alkoxyphenyl groups, $NiS_4C_4(p\text{-}n\text{-}C_9H_{19}O\text{-}Ph)_4$ (6a) and $NiS_4C_4(p\text{-}n\text{-}C_{11}H_{23}O\text{-}Ph)_4$ (6b), exhibit discotic mesomorphism as mentioned above. The half-wave po-

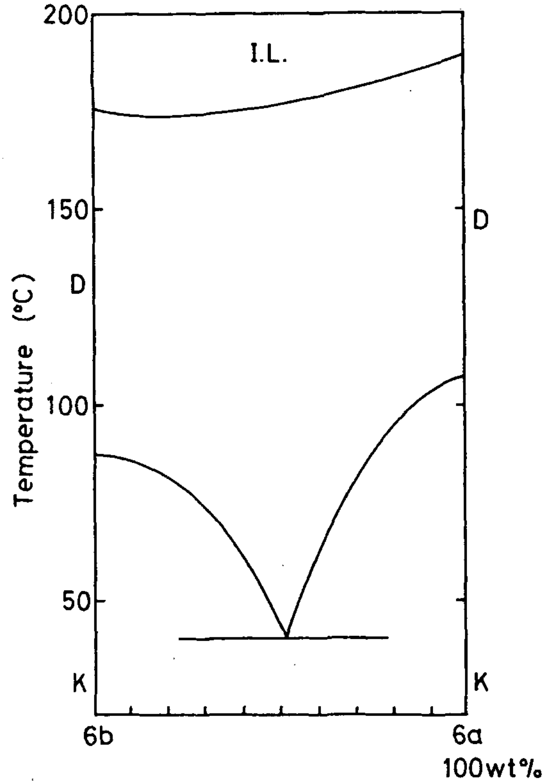


FIGURE 1 Miscibility diagram for the complexes (6a) and (6b).

tentials for reduction of these complexes are −0.06V for (6a) and −0.07V for (6b). The potentials are somewhat less positive than those of the corresponding core complex $NiS_4C_4Ph_4$ (+0.03V). The complexes (6a,b) are, however, thought to be fairly good π-acceptors, comparable to haloanils (chloranil, bromanil, and fluoranil).[15] They have a possibility to be applied to one-dimensional organic conductors.

EXPERIMENTAL SECTION

The phase transformation behavior of these complexes was observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and 82, and measured with differential scanning calorimeters, Rigakku Denki Thermoflex TG-DSC and Rigaku Denki Thermoflex DSC-10A. Using these differential

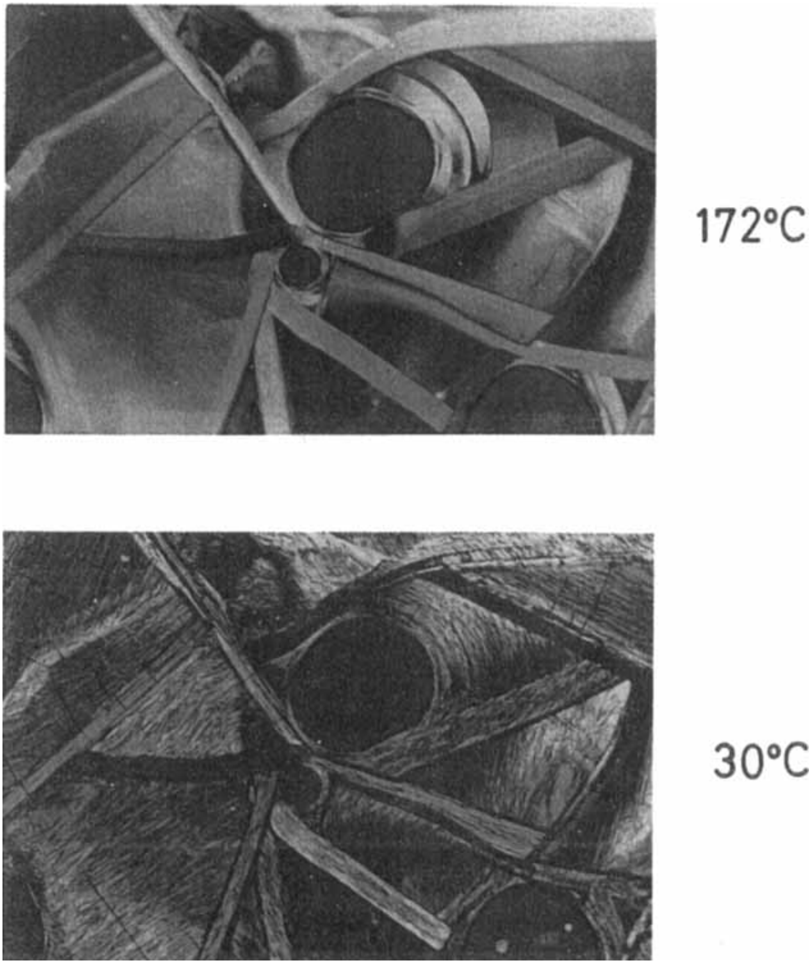


FIGURE 2 Photomicrographs of the mesomorphic state at 172°C and the K$_1$ crystalline state at 30°C for the complex (6b).

scanning calorimeters, miscibility tests were carried out between the complexes (6a) and (6b). Since these mesophases are very viscous fluids, the mixing of them was made when both were in the states of isotropic liquid of the two complexes; the samples measured here were prepared by heating at 195°C for 2 hours followed by slow cooling to room temperature because each of the complexes (6a,b) does not decompose at the temperature lower than 210°C.

The electrochemical properties were determined in methylene chloride solutions containing 0.1 M tetrabuthylammonium perchlorate as supporting electrolyte. The solution concentrations of the metal com-

TABLE II

Cyclic voltammetric data obtained from bis-1,2-dithiolenes

Couple: $[ML_2]^0 + e^- \rightleftharpoons [ML_2]^{-1}$ (volts)

M	Ligands, L_2	CH_2Cl_2[a]	CH_3CN[b]
Ni	$S_4C_4H_4$		+0.09
	$S_4C_4(n-C_8H_{17})_4$	−0.22	
	$S_4C_4Ph_4$	+0.03[c]	
	$S_4C_4(p\text{-}n\text{-}C_9H_{19}OPh)_4$[d]	−0.06	
	$S_4C_4(p\text{-}n\text{-}C_{11}H_{23}OPh)_4$[e]	−0.07	

[a] vs. SCE, electrolyte Bu_4NClO_4; sweep rates 10 mV/sec; temperature = 25°C.

[b] J. A. McCleverty, "Progress in Inorganic Chemistry," S. J. Lippaard, Ed., John Wiley & Sons Inc., New York, 1968, Vol. 10, p. 86: vs. standard calomel electrode.

[c] The value reported in the above reference is +0.01V.

[d] Complex (6a) in this paper.

[e] Complex (6b) in this paper.

plexes were 3.02×10^{-3} M for (6a) and 3.08×10^{-3} M for (6b). Cyclic voltammograms were obtained with a Yanagimoto Polarographic Analyzer P-1100 and recorded with a Graftec X-Y recorder WX4422. The measurements were made at a glassy-carbon working electrode vs. a saturated calomel electrode (SCE).

Since the complex (6b) was synthesized in the same manner as the complex (6a), the following detailed procedures are presented only for the case of (6a).

p-n-Nonyloxybromobenzene (2a)

To a solution of 85% purity of potassium hydroxide (9.2 g, 0.14 mol) in ethanol (150 ml) was added dropwise p-bromophenol (20.0 g, 0.12 mol) and then a solution of n-nonylbromide (26.6 g, 0.13 mol) in ethanol (50 ml). The mixture was refluxed by stirring for 12 hrs. It was then extracted with ether, and the organic extract was washed with water and dried over sodium sulfate. After evaporation of the ether, the residue was distilled under reduced pressure to give 27.9 g of *2a* (b.p. = 129.0°C at 0.20 mmHg, colorless oil); yield 80.4%. IR (liquid film) ν CH_2 2950 and 2850 cm^{-1}: ^1H-NMR ($CDCl_3$): δ 0.87(t, J=5 Hz, 3H), 1.27(m, 14H), 3.76(t, J=5 Hz, 2H), 6.61(d, J=9 Hz, 2H), and 7.23(d, J=9 Hz, 2H).

4,4′-Di(n-nonyloxy)stilbene (4a)

Dry tetrahydrofuran (THF) (20 ml) was poured on magnesium turning (2.23 g, 92 m atom) in a flask under a nitrogen atmosphere. A small portion of mixture of p-n-nonyloxy-bromobenzene (25.0 g, 84 mmol) and 40 ml of THF was run in and the flask refluxed gently until the reaction started. After the reaction had started, the rest of the mixture was added dropwise while stirring. When the addition was complete the refluxing was continued for 12 hrs.

After the flask had been cooled by immersion in ice water, a catalytic amount of dichloro[1,2-bis(diphenyl-phosphino)ethane] nickel(II), [$NiCl_2$(dpe)], (0.14 g, 0.25 mmol) was added and then trans dichlorethyrene (4.05 g, 42 mmol) was added dropwise. When the addition was complete the stirring was kept up for 10 min. To complete the reaction it was refluxed for 20 hrs. The reaction mixture was then cooled to room temperature and a dilute aqueous solution of hydrochloric acid was added. The resulting solid was filtered to give crude *cis* 4,4′-di(n-nonyloxy)stilbene (4a) (11.8 g). The filtrate was extracted with ether and dried over sodium sulfate. The solvent was evaporated to give a crude trans-form of (4a) (0.1 g). The crude yield was 61% for cis- and trans-isomers of (4a). Recrystallization of the cis-form from THF gave 10.3 g of white plates in 53% yield. Recrystallization of the trans-form from ethyl acetate gave a slightly yellow powder.

cis (*4a*); m.p. = 150 – 151°C; I.R. (KBr) 2925, 2860, 1600, 1500, 1460, 1250, 1170, 1110, 1010, 950, 820 cm^{-1}; ^{1}H-NMR: no solvents to resolve this compound at room temperature.

trans (*4a*); this form has a mesomorphic property: 96°C (Crystal → Smectic phase) and 109°C (Smectic phase → isotropic liquid); I.R. (KBr) 2920, 2850, 1600, 1495, 1465, 1250, 1170, 1030, 1010, 820, 800 cm^{-1}.

1,2-Di(p-n-nonyloxyphenyl)ethane-1,2-dione(5a)

To a mixture of cis 4,4′-di(n-nonyloxy)stilbene (6.0 g, 13 mmol) and selenium dioxide (3.2 g, 28 mmol) was added 300 ml of 80% aqueous acetic acid and 3 ml of conc. sulfuric acid. The mixture was refluxed by stirring for 17 hrs. The resulting selenium powder was removed by filtration. The filtrate was extracted by ether and washed with water until it was neutral, dried over sodium sulfate. Evaporation gave 6.0 g of crude (5a) (brown solid), which was purified by recrystallization from n-hexane to afford 2.1 g (33%) of a grayish green powder. Anal. Found (Calcd. for $C_{32}H_{46}O_4$): C 77.51% (77.69), H 9.30% (9.37). MS(m/e): 494 (M^+). I.R. (KBr) 2900, 2850, 1650, 1590, 1470, 1250, 1220, and 1160 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.87 (t, J = 4 Hz, 6H), 1.30 (m, 28H), 3.97 (t, J = 6 Hz, 4H), 6.83 (d, J = 9 Hz, 4H), and 7.81 (d, J = 9 Hz, 4H). This compound exhibits the so-called "double melting behavior"[16]: m.p. = 60 and 68°C.

Bis[1,2-di(p-n-nonyloxyphenyl)ethane-1,2-dithione]nickel(6a)

A mixture of 1,2-di(p-n-nonyloxyphenyl)ethane-1,2-dione (1.8 g, 3.6 mmol), phosphorous pentasulfide (1.2 g, 5.5 mmol), and 30 ml of dioxane was refluxed for 5 hrs. The hot reaction mixture was filtered to remove the unreacted phosphorous pentasulfide and washed with a small portion of hot dioxane several times. To the filtrate was added nickel(II) dichloride hexahydrate (0.48 g, 2.0 mmol) in 10 ml of water and the reaction mixture was refluxed for 2 hrs. After the reaction mixture had been cooled by immersion in ice water, a black powder was formed and was collected by filtration to give 1.4 g of the crude complex (6a). Purification was performed by recrystallization from ethyl acetate to afford 1.1 g of black needle-like crystals, yield 57%. Anal. Found (Calcd. for $C_{64}H_{92}O_4S_4Ni$): C 69.37% (69.10), H 8.35% (8.34). ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.87 (t, J=4 Hz, 12H), 1.31 (m, 56H), 3.88 (t, J=6 Hz, 8H), 6.56 (d, J=8 Hz, 8H), and 7.19 (d, J=8 Hz, 8H), IR (KBr) 2930, 2860, 1600, 1510, 1470, 1360, 1300, 1250, 1170, 1140, and 880 cm^{-1}, λmax ($CHCl_3$) 928 (ϵ 33700), 625 (2480), 468 (shoulder, 4260), 337(sh., 28900), 301(44500), and 285 nm (sh., 40600).

Acknowledgment

This work was partially supported by the Joint Studies Program (1986–1986) of the Institute for Molecular Science. We are grateful to T. Koyama for his help in the measurements of cyclic voltammetry.

References

1. For part 3 see: K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, in the press.
2. (a) S. Chandrasekhar, "Advances in Liquid Crystals," G. H. Brown, ed., Vol. 5, Academic Press, London, pp. 47–78 (1982). (b) S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **63**, 171 (1981).
3. J. Martinsen, L. H. Pace, T. E. Phillips, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, **104**, 83 (1982).
4. (a) C. Destrade, P. Foucher, H. Gasparoux and Nguyen Huu Tinh, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984). (b) quite recently, the discogenes having non-flat cores have been reported: A.-J. Lehn, J. Malthete, and A.-M. Levelut, *J. Chem. Soc., Chem. Commun.*, **1794** (1985).
5. C. Piechoki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, **104**, 5245 (1982).
6. (a) H. Strzelecka, V. Gionis, J. Rivory and S. Flandrois, *J. Physique.*, **44**, C3, 1201 (1983). (b) F. D. Saeva, G. A. Reynolds and L. Kaszczuk, *J. Am. Chem. Soc.*, **104**, 3524. (1982). (c) V. Gions, R. Fugnitto, G. Meyer, H. Strzelecka and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **90**, 153 (1982).
7. In the following paper, the disc-like Compound 4 exhibits mesomorphism although it has not been established to be a discotic mesogen: M. Veber, R. Fugnitto and H. Strzelecka, *Mol. Cryst. Liq. Cryst.*, **96**, 221 (1983).

8. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).
9. N. Sonoda, Y. Yamamoto, S. Murai and S. Tsutsumi, *Chem. Lett.*, **229** (1972).
10. K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972).
11. W. R. Young, I. Haller and A. Aviram, *Mol. Cryst. Liq. Cryst.*, **15**, 311 (1972).
12. R. E. Rondeau, M. A. Berwick, R. N. Steppel and M. P. Serve, *J. Am. Chem. Soc.*, **94**, 1096 (1972).
13. K. Ohta, H. Muroki, A. Takagi, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **135**, 247 (1986).
14. Only a few organic transition metal complexes exhibit discotic mesomorphism. All of the complexes known to date are copper(II) complexes exept for Compound 4 in Ref. 7: (a) A. M. Giroud-Godquin and J. Billard, ibid., **66**, 147 (1981). ibid., **97**, 287 (1983). (b) K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *J. Chem. Soc. Chem. Commun.*, **1099** (1984). K. Ohta, A. Ishii, H. Muroki, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **116**, 299 (1985). (c) Ref. 12 & Ref. 1. in this paper. (d) A. M. Giroud-Godquin, G. Sigaud, M. F. Achard and F. Hardouin, *J. Physique Lett.*, **45**, L-385 (1984)(e) Ref. 5 in this paper. (f) A. M. Giroud-Godquin, J. C. Marchon, D. Guillon and A. Skoulios, *J. Physique Lett.*, **45**, L-681 (1984).
15. See Figure 1 in the following paper: J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, **126**, 55 (1985).
16. The multiple-melting behavior of glycerides is well known: D. Chapman, *Chem. Rev.*, **62**, 433 (1962).