Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Discotic Liquid Crystals of Transition Metal Complexes 11[1]: The First π-Acceptor in Discotic Columnar Liquid Crystals Obtained from Octasubstituted Bis(diphenylethane-1,2-dithiolene)nickel Complexes

Kazuchika Ohta [a], Hiroshi Hasebe [a], Hiroshi Ema [a], Mitsuo Moriya [a], Tetsuya Fujimoto [a] & Iwao Yamamoto [a]
[a] Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386, Japan
Version of record first published: 24 Sep 2006.

To cite this article: Kazuchika Ohta , Hiroshi Hasebe , Hiroshi Ema , Mitsuo Moriya , Tetsuya Fujimoto & Iwao Yamamoto (1991): Discotic Liquid Crystals of Transition Metal Complexes 11[1]: The First π-Acceptor in Discotic Columnar Liquid Crystals Obtained from Octasubstituted Bis(diphenylethane-1,2-dithiolene)nickel Complexes, Molecular Crystals and Liquid Crystals, 208:1, 21-32

To link to this article: http://dx.doi.org/10.1080/00268949108233940

Mol. Cryst. Liq. Cryst., 1991, Vol. 208, pp. 21–32
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Discotic Liquid Crystals of Transition Metal Complexes 11[1]: The First π-Acceptor in Discotic Columnar Liquid Crystals Obtained from Octasubstituted Bis(diphenylethane-1,2-dithiolene)nickel Complexes

KAZUCHIKA OHTA*, HIROSHI HASEBE, HIROSHI EMA, MITSUO MORIYA, TETSUYA FUJIMOTO, and IWAO YAMAMOTO

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

(Received March 22, 1991; in final form May 27, 1991)

Disk-like complexes, bis[1,2-di(3′,4′-di-n-alkylphenyl)ethane-1,2-dithiolene]nickel (n-alkyl = n-hexyl, n-octyl) and bis[1,2-di(3′,4′-di-n-decyloxyphenyl)ethane-1,2-dithiolene]nickel have been synthesized and characterized. It was found that n-decyloxy derivative exhibits a hexagonal disordered columnar (D_{hd}) mesophase while n-alkyl derivatives are not discotic liquid crystals but isotropic liquids at room temperature. The half-wave potentials for reduction of these complexes is $-0.04 \sim -0.06$V. n-Decyloxy derivative is the first π-acceptor in discotic columnar liquid crystals.

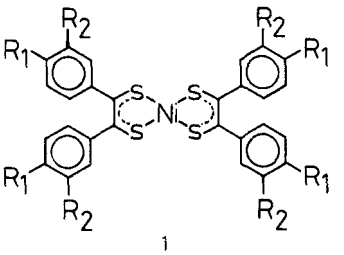
1. INTRODUCTION

Discotic columnar mesogens consist of a central disk-like rigid core surrounded by several flexible long alkyl chains; these disk-like cores pile up to form columns in mesophase. Because of the column structure, discotic columnar discogens can be applied to one-dimensional conductors.[2,3]

Only π-donor columnar mesogens have been studied for the application so far,[4–9] because π-acceptor columnar discogens have not been reported. Therefore, it is desired to obtain the π-acceptor columnar discogen.

One of the ways to obtain the π-acceptor columnar discogen is to introduce several alkyl and/or alkoxy chains into bis(dithiolene)nickel complexes, because the core complex is well known to be a good π-acceptor.[10]

We have synthesized tetra-alkyl substituted bis(dithiolene)nickel complexes (**1a**) and tetra-alkoxy substituted bis(dithiolene)nickel complexes (**1b**), and found that these complexes (**1a**) and (**1b**) have a unique discotic lamellar (D_L) mesophase.[11–13] Although these complexes are the first π-acceptors in discogens, they are not discotic *columnar* but discotic *lamellar* mesogens.[14] Thereby, we have syn-



1

[a] R_1=n-C_nH_{2n+1}(n=8~12), R_2=H

[b] R_1=n-$C_nH_{2n+1}O$(n=7~12), R_2=H

[c] R_1=R_2=n-C_nH_{2n+1}(n=6,8)

[d] R_1=R_2=n-$C_{10}H_{21}O$

thesized *octa-alkyl* substituted bis(dithiolene)nickel complexes (**1c**) and an *octa-alkoxy* substituted bis(dithiolene)nickel complex (**1d**) in an attempt to obtain discotic columnar mesogens. As a result, it was found that the complexes (**1c**) are not discotic liquid crystals but an isotropic liquids at room temperature, and that the complex (**1d**) is the first π-acceptor discotic columnar liquid crystal. We wish to report here the synthesis and physical properties of the complexes (**1c**,**d**).

2. RESULTS AND DISCUSSION

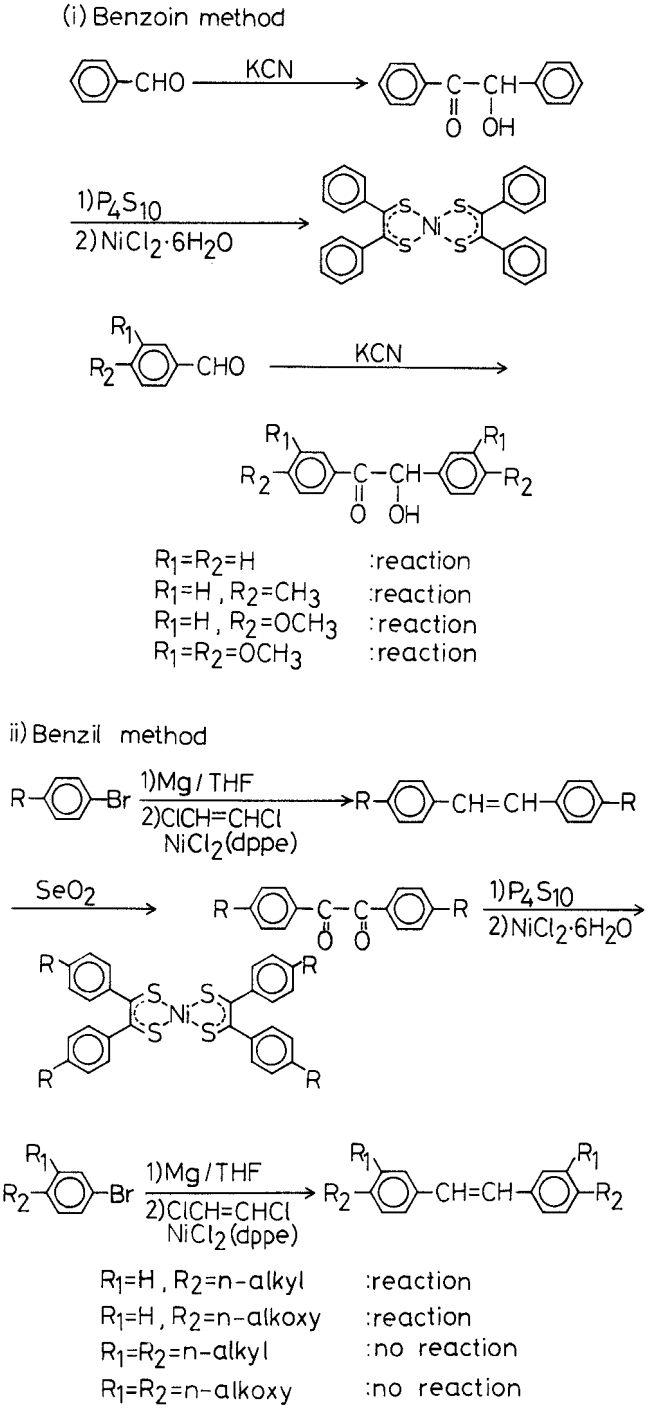
2.1 Synthesis

In order to obtain alkyl and/or alkoxy substituted bis(dithiolene)nickel complexes, the corresponding benzoin, benzil or acyloin must be prepared as the precursors (Scheme I).

The unsubstituted complex, bis(1,2-diphenylethane-1,2-dithiolene)nickel complex has been prepared from benzoin by the method of Schrauzer *et al.*[15] However, this method cannot be adopted for the long-chain substituted complexes, because one cannot obtain the long-chain-substituted benzoins except for dimethyl-, dimethoxy- and tetramethoxy-benzoins (Scheme I (i): Benzoin method).

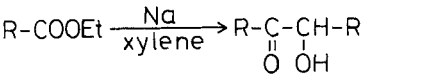
We overcame the limitation of the Benzoin method, and succeeded in obtaining the *tetra-alkyl and/or tetra-alkoxy* substituted bis(dithiolene)nickel complexes by using the corresponding benzils as the precursors (Scheme I (ii): Benzil method).[16,17] Nevertheless, it is still impossible to obtain the *octa-alkyl and/or octa-alkoxy* substituted bis(dithiolene)nickel complexes by this benzil method (Scheme I (ii)).

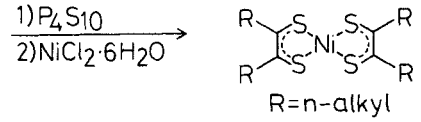
We could synthesize the *tetra-alkyl* substituted benzoins by using acyloin condensation which is generally utilized not for arylic ester but for alphatic ester (Scheme I (iii): Acyloin method), and synthesized the corresponding octa-alkyl substituted bis(dithiolene)nickel complexes (**1c**) (Scheme II). Even by this acyloin

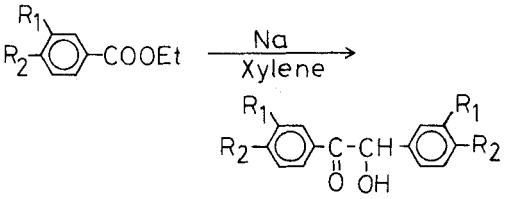


SCHEME I Synthetic routes of the various substituted bis(dithiolene)nickel complexes: (i) benzoin method, (ii) benzil method, and (iii) acyloin method.

iii) Acyloin method



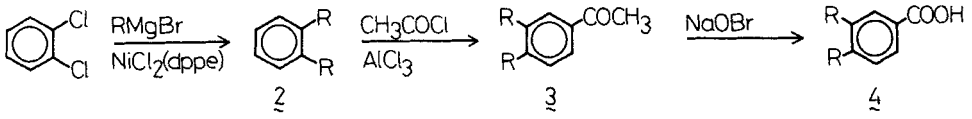


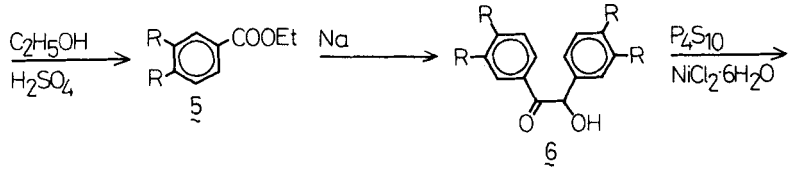


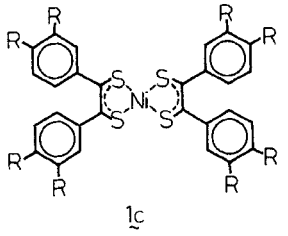
$R_1 = R_2 = CH_3, C_6H_{13}, C_8H_{17}, C_{12}H_{25}$: reaction

$R_1 = R_2 = C_{10}H_{21}O, C_{12}H_{25}O$: no reaction

SCHEME I (*Continued*)







SCHEME II Synthetic route of the octa-alkyl-substituted bis(dithiolene)nickel complexes (**1c**).

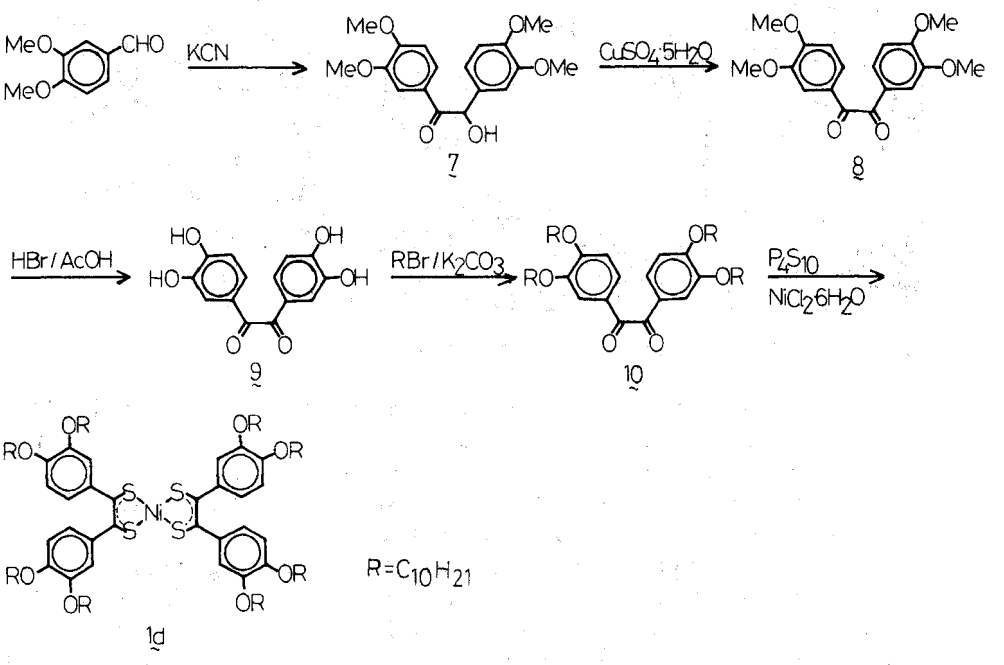
method, the preparation of *tetra-alkoxy* substituted benzoins was unsuccessful (Scheme I (iii)).

Therefore, we attempted to utilize the synthetic route of 3,3′,4,4′-tetrapentyloxybenzil ((10) in Scheme III) reported by Wenz[18] (Scheme III). As a result, we succeeded for the first time in obtaining 3,3′,4,4′-tetradecyloxybenzil (10) and the corresponding octadecyloxy substituted bis(dithiolene)nickel complex (**1d**).

2.2 Mesomorphic Properties of the Complex (1d)

It is found that the complex (**1d**) has a discotic columnar mesophase. In Table I are summarized the phase transition temperatures and enthalpy changes for the complexes (**1c**, **d**) measured by a DSC and a polarizing microscope.

When the virgin microcrystals were heated up from room temperature at the heating rate of 10°C/min. under the polarizing microscope, they were transformed at 84°C into a viscous liquid with birefringence, which is one of the characteristics of liquid crystalline phases. On further heating, it cleared into an isotropic liquid at 112°C. When the isotropic liquid was cooled down at the cooling rate of −10°C/min., a fan-shaped texture appeared at 110°C (Figure 1). Generally, the texture is often observed in hexagonal disordered columnar mesophase (D_{hd}).[19] On further cooling, the texture remained even till room temperature. This is due to the supercooling of the mesophase without crystallization. This behavior could be observed also by a DSC. The DSC thermogram of the virgin sample at the heating rate of 10°C/min. gave two endothermic peaks at 84°C and 112°C. However, when it was heated over the clearing point of 112°C and then cooled down to room



SCHEME III Synthetic route of the octa-decyloxy-substituted bis(dithiolene)nickel complex (**1d**).

TABLE I

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes (**1c**, **d**)

	T_t(°C)[ΔH_t(kcal/mol)] Phase ⟶ Phase[a]
1c	$\begin{pmatrix}\text{n-hexyl}\\ \text{n-octyl}\end{pmatrix}$ I.L. at room temperature
1d	K $\underset{}{\overset{84[31.1]}{\rightleftharpoons}}$ Dhd $\underset{}{\overset{112[2.62]}{\rightleftharpoons}}$ I.L.

[a] Phase nomenclature: K = crystal, D_{hd} = hexagonal disordered columnar mesophase, and I.L. = isotropic liquid.

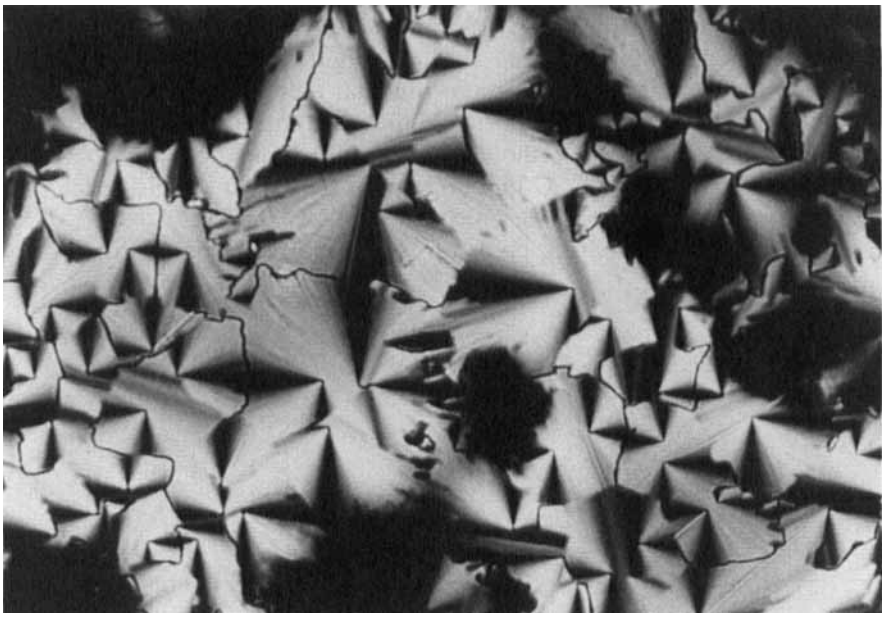


FIGURE 1 Photomicrograph of D_{hd} in the complex (**1d**) at 110°C. See Color Plate III.

temperature, the DSC thermogram of this sample gave only one peak at 112°C for the second heating run from room temperature to 120°C. This means that the supercooled discotic mesophase can be easily obtained at room temperature.

The identification of the discotic mesophase was performed by using an X-ray diffraction powder pattern at mesomorphic temperature.

The X-ray diffraction pattern at room temperature gave a large numer of sharp reflections which are compatible with the characteristic of crystalline order. On the other hand, the X-ray diffraction pattern of the discotic mesophase gave three narrow reflections at d = 28.2Å, d = 16.5Å and d = 14.4Å, which can be assigned to (100), (110), and (200) in a two-dimensional hexagonal lattice, respectively. The

lattice constant is a = 32.7Å. The pattern also gave a halo at d ≃ 4.4Å (2θ ≃ 20°), which corresponds to the melt of the alkyl chains (Figure 2). Therefore it could be assigned from these results that the complex (**1d**) has a D_{hd} columnar mesophase. This assignment is consistent with that of microscopic observations of the textures mentioned above.

2.3 Electrochemistry

In Table II are summarized the half-wave potentials for reduction of the non-discogen of the octa-alkyl-substituted bis(dithiolene)nickel complexes (**1c**) and the discogen of the octadecyloxy-substituted bis(dithiolene)nickel complex (**1d**). As can be seen from Table II, the difference of the reduction potentials among these complexes is quite small. Therefore, it is obvious that the substituents' effect is not on electrochemical properties but on mesomorphic properties. The value of the potential, $-0.04 \sim -0.06$ V is somewhat less positive than the corresponding unsubstituted core complex, $Ni_4S_4C_4Ph_4$.[17] The complexes (**1c**) and (**1d**) are, how-

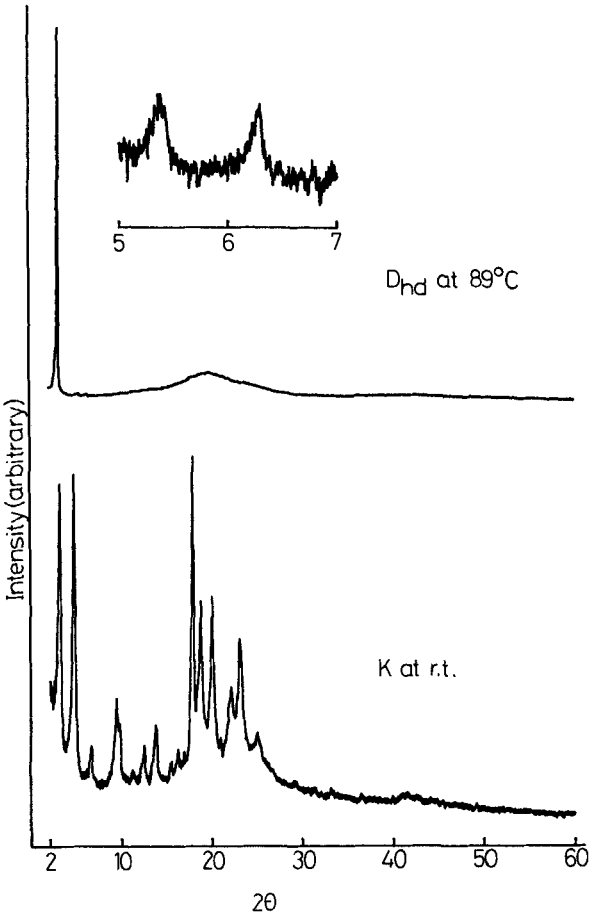


FIGURE 2 X-ray diffraction powder patterns of the complex (**1d**).

TABLE II

Cyclic voltammetric data obtained from octasubstituted bis(dithiolene)nickel complexes

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

Compound	Substituents	Volts (vs. SCE in CH_2Cl_2)
1c	$R_1{=}R_2{=}C_6H_{13}$	−0.04
	$R_1{=}R_2{=}C_8H_{17}$	−0.06
1d	$R_1{=}R_2{=}C_{10}H_{21}O$	−0.06

ever, thought to be fairly good acceptors, comparable to haloanils (chloranil, bromanil, and fluoranil).[20]

3. CONCLUSION

Disk-like complexes, bis[1,2-di(3′,4′-di-n-alkylphenyl)ethane-1,2-dithiolene]nickel (n-alkyl = n-hexyl, n-octyl) and bis[1,2-di(3′,4′-di-n-decyloxyphenyl)ethane-1,2-dithiolene]nickel, have been synthesized and characterized. The only decyloxy substituted complex has a hexagonal disordered columnar (D_{hd}) mesophase between 84°C and 112°C. The half-wave potential for reduction of these complexes is −0.04 ~ −0.06 V (vs. SCE in dichloromethane solution). The decyloxy substituted complex is the first π-acceptor in discotic columnar mesogens.

4. EXPERIMENTAL

4.1 Synthesis of the Octa-n-alkyl Substituted Complexes (1c)

The synthetic route of the n-alkyl substituted complexes (**1c**) is shown in Scheme II. Since the n-hexyl substituted complex was synthesized in the same manner as the n-octyl substituted complex, the following detailed procedures are presented only for the case of the n-octyl derivative.

o-Di-n-octylbenzene (**2**). Dry tetrahydrofuran (THF) (20 ml) was poured on magnesium turnings (8.38 g, 0.35 mol) in a flask under a nitrogen atmosphere. A small portion of a mixture of n-octylbromide (60.8 g, 0.32 mol) and 100 ml of THF was run in the flask and refluxed gently until the reaction started. After the reaction started, the rest of the mixture was added dropwise with stirring. When the addition was complete, the refluxing was continued for 4 hrs.

After the flask had been cooled by immersion in an ice water bath, a catalytic amount of dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II), [$NiCl_2$(dppe)], (0.91 g, 1.7 mmol) was added and then o-dichlorobenzene (22.05 g, 0.15 mol) was added carefully dropwise. When the addition was complete, the stirring was continued for 1 hr. To complete the reaction it was refluxed for 12 hrs. The reaction mixture

was then cooled to room temperature and a dilute aqueous solution of hydrochloric acid was added. The reaction mixture was extracted with ether, and dried over sodium sulfate. After evaporation of the ether, the residue was distilled under reduced pressure to give 18.0 g of (1) (b.p. = 191.5°C at 0.15 mmHg, colorless oil). Yield 39.6%. I.R. (liquid film, cm^{-1}), 2950, 2880. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.9(t, 6H), 1.3(m, 24H), 2.6(t, 4H), 7.1(s, 4H).

3,4-Di-n-octylacetophenone (**3**). Dry dichloromethane (CH_2Cl_2) (100 ml) was poured into a flask under a nitrogen atmosphere and cooled down to −76°C in a dry ice-acetone. $AlCl_3$ (16.66 g, 0.13 mol) was added in the flask. A mixture of acetyl-chloride (9.77 g, 0.13 mol) and 20 ml of CH_2Cl_2 was poured into the flask, and a mixture of o-di-n-octylbenzene (**2**) (21.0 g, 66 mmol) and 20 ml of CH_2Cl_2 was added dropwise with stirring. When the addition was complete, the stirring was continued for 6 hrs. After the reaction was complete, the reaction mixture was poured into a beaker with ice-HCl aqueous solution and extracted with CH_2Cl_2. Evaporation gave 23.3 g of 3,4-di-n-octyl-acetophenone, which was not purified because this product was sufficiently pure. TLC(silica gel, $CHCl_3$, Rf = 0.69, single spot). Yield 100%. I.R. (liquid film, cm^{-1}), ν(C═O) = 1690. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.9(t, 6H), 1.3(m, 24H), 2.6(t, 4H), 2.5(s, 3H), 6.9 ~ 7.7(m, 3H).

3,4-Di-n-octylbenzoic acid (**4**). In a flask was placed a solution of sodium hydroxide (21.1 g, 0.32 mol) in 180 ml of water, and the solution was cooled to 0°C in an ice-salt bath. To the well-stirred solution, bromine (31.6 g, 0.20 mol) was added at such a rate as to keep the temperature below 10°C. The solution was cooled again to 0°C, and 3,4-di-n-octylacetophenone (22.0 g, 66 mmol) was added, the temperature being kept below 10°C. After the solution was decolorized it was stood with stirring for 3 hrs. at room temperature. An aqueous solution of $NaHSO_3$ was added and an aqueous solution of hydrochloric acid was added (until pH 3 ~ 4). The reaction mixture was extracted with ether and dried over sodium sulfate. The solvent was evaporated to give a crude 3,4-di-n-octylbenzoic acid (25.6 g). This product was purified by column chromatography using silica gel (CH_2Cl_2, Rf = 0.12) to give 14.2 g of the pure (**4**). Yield 64.1%. I.R. (liquid film, cm^{-1}), ν(C═O) = 1670. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.9(t, 6H), 1.3(m, 24H), 2.6(t, 6H), 6.9 ~ 7.7(m, 3H).

Ethyl 3,4-di-n-octylbenzoate (**5**). Ethanol (300 ml) and 3,4-di-n-octylbenzoic acid (**4**) (13.0 g, 39 mmol) were poured in a flask and refluxed. Then conc. H_2SO_4 (25.3 ml, 46 mmol) was added dropwise with stirring. When the addition was complete the refluxing was continued for 6 hrs. The reaction mixture was poured onto crushed ice and extracted with ether. The solvent was evaporated and then the residue was distilled under reduced pressure to give 7.5 g of ethyl 3,4-di-n-octylbenzoate (b.p. = 153°C at 0.06 mmHg). Yield 53%. I.R. (liquid film, cm^{-1}), ν(—COO—) = 1720. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.9(t, 6H), 1.3(m, 26H), 1.5(t, 3H), 2.6(t, 4H), 4.3(q, 2H), 6.9 ~ 7.7(m, 3H).

3,3',4,4'-Tetra-n-octylbenzoin (**6**). Dry xylene (50 ml) was poured on sodium (1.58 g, 69 mmol) in a flask under a nitrogen atmosphere and heated to reflux. Sodium dispersion was obtained at b.p. of xylene and then cooled down to about 100°C.

Ethyl 3,4,-di-n-octylbenzoate (**5**) in 50 ml of dry xylene was added dropwise with stirring. The reaction temperature was kept at about 100°C and the stirring was continued for 20 hrs. When the reaction was complete the reaction mixture was cooled to room temperature. Ethanol (20 ml) was carefully added and then a dilute aqueous solution of hydrochloric acid was added. The reaction mixture was extracted with ether, and dried over sodium sulfate. After evaporation of the ether, the residue was purified by column chromatography using silica gel ($CHCl_3$, Rf = 0.52) to give 2.8 g of (**6**). Yield 31%. I.R. (liquid film, cm^{-1}), ν(C=O) = 1680, ν(OH) = 3500. ^{1}H-NMR($CDCl_3$, TMS) δ(ppm), 0.9(t, 12H), 1.3(m, 52H), 2.5(t, 8H), 4.5(d, 1H), 5.8(d, 1H), 6.9 ~ 7.7(m, 6H).

Bis[1,2-di(3',4'-di-n-octylphenyl)ethane-1,2-dithiolene]nickel (**1c**). A mixture of 3,3',4,4'-tetraoctylbenzoin (**6**) (2.0 g, 3.8 mmol), phosphorous pentasulfide (3.36 g, 7.6 mmol) and 40 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 (0.45 g, 1.9 mmol) in 10 ml of ethanol and the reaction mixture was refluxed for 2 hrs. After the reaction mixture had been cooled to room temperature, a green-black liquid was formed and extracted with benzene. The benzene solution was dried over sodium sulfate. After evaporation of the benzene, the residue was purified by silica gel column chromatography (n-hexane, Rf = 0.14) to give 0.39 g of (**1c**). Yield 30%. I.R. (liquid film, cm^{-1}), 2950, 2875, 1605, 1500, 1476, 1360, ν(C=S) = 1125. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.9(t, 24H), 1.3(m, 96H), 2.5(t, 16H), 7.2 ~ 7.5(m, 12H). Electronic spectra [in $CHCl_3$, λmax(nm) (logε)], 898(4.52), 323(4.60), 278(4.58), 620(3.31).

4.2 Synthesis of the Octa-n-decyloxy Substituted Complex (1d)

Synthesis of the complex (1d) was carried out using the method illustrated in Scheme III. The precursors (**7**) through (**10**) were prepared by the method of Wenz.[18]

3,3',4,4'-Tetramethoxybenzoin (**7**). Pottasium cyanide (1.72 g, 26.0 mmol) was dissolved in 10 ml of water. To this solution, 3,4-dimethoxybenzaldehyde (10.0 g, 60.0 mmol) and 18 ml of ethanol were added. Under the nitrogen atmosphere, the reaction mixture was refluxed with stirring for 50 hrs. The mixture was extracted with chloroform, and the organic layer was washed with water, and then dried over sodium sulfate. The chloroform was evaporated to give a yellowish brown viscous liquid. Purification was not carried out. Yield 74%. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm) 3.43 ~ 4.50(m, 13H), 5.76 ~ 7.46(m, 7H), 9.81(—CHO of unreacted 3,4-dimethoxybenzaldehyde). I.R. (liquid film, cm^{-1}) 3450, 2950, 2850, 1650, 1590, 1505, 1270.

3,3',4,4'-Tetramethoxybenzil (**8**). A solution of crude 3,3',4,4'-tetramethoxybenzoin (7.39 g, 22.0 mmol) in 40 ml of pyridine was poured into an aqueous solution of copper(II) sulfate pentahydrate (16.5 g, 66.0 mmol) in 30 ml of water. The reaction mixture was refluxed with stirring for 7 hrs. 40 min. After the mixture had been cooled down to room temperature, the target compound (**8**) partially crystallized from the mixture. To this was added 50 ml of water, and then the

resulting crystals were collected by filtration and washed with water several times to give 2.40 g of yellow needle-like crystals. Yield 33%. M.p. 226°C. Purification was not carried out. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 3.88(s, 12H), 6.73 ~ 7.50(m, 6H). I.R. (KBr pellet, cm^{-1}), 2950, 2850, 1660, 1590, 1510, 1270.

3,3',4,4'-Tetrahydroxybenzil (**9**). Crude 3,3',4,4'-tetramethoxybenzil (2.40 g, 7.30 mmol) was dissolved in a mixture of 130 ml of glacial acetic acid and 130 ml of 47%-hydrobromic acid. It was refluxed with stirring for 10 hrs. under a nitrogen atmosphere. To this resulting reaction mixture, was added 600 ml of water and then it was extracted with diethylether. The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated to give 1.77 g of yellow solid. Yield 88%. Purification was not carried out. I.R. (film, cm^{-1}), 3350, 1650, 1595, 1510, 1300.

3,3'-4,4'-Tetra-n-decyloxybenzil (**10**). A solution of crude 3,3',4,4'-tetrahydroxybenzil (1.77 g, 6.50 mmol) in 40 ml of N,N-dimethylacetamide was poured on anhydrous potassium carbonate (3.59 g, 26.0 mmol) and 1-bromodecane (5.75 g, 26.0 mmol). The reaction mixture was heated at 70°C for 17 hrs. under a nitrogen atmosphere. The mixture was extracted with dichloromethane, the organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated to give 24.13 g of yellow solid. Purification was carried out by recrystallization from ethyl acetate to afford 4.06 g of white micro needle-like crystals. Yield 74%. M.p. 96°C. Anal. Found (Calcd. for $C_{54}H_{90}O_6$): C 77.98%(77.65), H 10.88%(10.86). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.87(t, J = 4Hz, 12H), 1.29 ~ 1.81(m, 64H), 4.00(t, J = 6Hz, 8H), 6.64 ~ 7.47(m, 6H). I.R. (KBr pellet, cm^{-1}), 2930, 2860, 1670, 1590, 1510, 1270.

Bis[1,2-di(3',4'-di-n-decyloxyphenyl)ethane-1,2-dithiolene]nickel (**1d**). A mixture of 3,3',4,4'-tetra-n-decyloxybenzil (3.00 g, 3.60 mmol), phosphorus pentasulfide (3.46 g, 16.0 mmol), and 100 ml of 1,4-dioxane was refluxed for 5 hrs. under a nitrogen atmosphere. The hot reaction mixture was filtrated to remove the unreacted phosphorus pentasulfide, which was washed with a small portion of hot 1,4-dioxane several times. To the filtrate was added nickel(II) dichloride hexahydrate (0.48 g, 2.0 mmol) in 20 ml of ethanol. The reaction mixture was refluxed for 2 hrs. under a nitrogen atmosphere. The reaction mixture was washed in a separatory funnel with water (0.8 litrex2) without using an organic solvent. The supernatant was next filtrated and washed with water. The supernatant was dissolved in 300 ml of chloroform and then dried over sodium sulfate. The chloroform was evaporated to give 3.12 g of dark green solid. Purification was carried out by column chromatography (silica gel, toluene: n-hexane = 5:4 (v/v), Rf = 0.56) and recrystallization from a mixed solvent of acetone and 2-propanol to give 1.32 g of grayish blue microcrystals. Yield 41%. Anal. Found (Calcd. for $C_{108}H_{180}O_8S_4Ni$): C 72.40(72.32), H 10.04(10.12). ^{1}H-NMR($CDCl_3$, TMS) δ(ppm), 0.89(t, J = 5Hz, 24H), 1.30 ~ 1.83(m, 128H), 3.77(t, J = 6Hz, 8H), 3.97(t, J = 6Hz, 8H), 6.67 ~ 7.09(m, 12H). I.R. (KBr pellet, cm^{-1}), 2950, 2870, 1600, 1520, 1370. Electronic spectrum [λ_{max} (log ε) in $CHCl_3$], 959nm(4.56), 659nm(shoulder, 3.44), 574nm(3.49), 368nm(shoulder, 4.40), 314nm(4.73).

4.2 Measurements

The phase transition behavior of the complex (**1d**) was observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with a differential scanning calorimeter, Rigaku Thermoflex TG-DSC. The X-ray diffraction powder patterns of the phases of the complex (**1d**) were measured with Cu-Kα radiation, using a Rigaku Geigerflex diffractometer equipped with a hand-made heating plate controlled by a thermoregulator.[21] The electrochemical property was determined in a dichloromethane solution containing 0.1M of tetrabutylammonium perchlorate as supporting electrolyte. Cyclic voltammogram was obtained with a Yanagimoto Polarographic Analyzer P-900 and recorded with a Graphtec X-Y recorder WX1000. The measurement was made at a glassy carbon-working electrode vs. a saturated calomel electrode (SCE).

Acknowledgment

This work was supported in part by a Grant-in-Aid from The Murata Science Foundation.

References

1. Part 10: K. Ohta, T. Watanabe, S. Tanaka, T. Fujimoto, I. Yamamoto, P. Bassoul, N. Kucharczyk, and J. Simon, *Liq. Cryst.*, in press.
2. T. J. Marks, *Science*, **227**, 881 (1985).
3. D. O. Cowan, and F. M. Wiygul, C & EN, 28 (1986).
4. C. Piechoki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, **104**, 5295 (1982).
5. H. Strzelecka, V. Gionis, J. Rivory, and S. Flandrois, *J. Physique*, **44**, C3-1201 (1983).
6. F. D. Saeva, G. A. Reynolds, and L. Kaszczuk, *J. Am. Chem. Soc.*, **104**, 3524 (1982).
7. V. Gionis, R. Fugnitto, G. Meyer, H. Strzelecka, and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **90**, 153 (1982).
8. V. Gionis, H. Strzelecka, and M. Veber, *Mol. Cryst. Liq. Cryst.*, **137**, 279 (1986).
9. L. Y. Chiang, J. P. Stockes, C. R. Safinya, and A. N. Broch, *Mol. Cryst. Liq. Cryst.*, **125**, 279 (1985).
10. J. A. McCleverty, "Progress in Inorganic Chemistry," S. J. Lippard, ed., Wiley-Interscience Publishers, John Willey & Sons Inc., New York, 1968, Vol. 10, p. 48–221.
11. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe and Y. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1986**, 883.
12. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe, and Y. Maruyama, *Mol. Cryst. Liq. Cryst.*, **147**, 15 (1987).
13. A. Takagi, 1987, Master thesis, Shinshu University, Ueda, Chap. 1,2.
14. K. Ohta, H. Hasebe, H. Ema, T. Fujimoto, and I. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1610 (1989); K. Ohta, unpublished results.
15. G. N. Schrauzer, and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).
16. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe, and Y. Maruyama, *J. Chem. Soc., Chem. Commun.*, 833 (1986).
17. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **147**, 15 (1987).
18. G. Wenz, *Makromol. Chem., Rapid Commun.*, **6**, 577 (1985).
19. C. Destrade, P. Foucher, H. Gasparoux, Nguyen H.T., A. M. Levelut, and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
20. J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, **126**, 55 (1985).
21. H. Ema, Master thesis, Shinshu University, Ueda, Chap. 7, 1988.