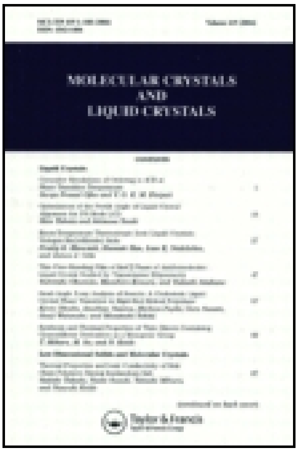

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Discotic Liquid Crystals of Transition Metal Complexes 12[1]: The Effect of the Alkoxy Chain Length on the Mesomorphism of Bis[1,2-di(3′,4′-di-n-alkoxyphenyl)ethane-1,2-dithiolene]nickel Complexes

Kazuchika Ohta [a] , Hiroshi Hasebe [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

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Discotic Liquid Crystals of Transition Metal Complexes 12[1]: The Effect of the Alkoxy Chain Length on the Mesomorphism of Bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dithiolene]nickel Complexes

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

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

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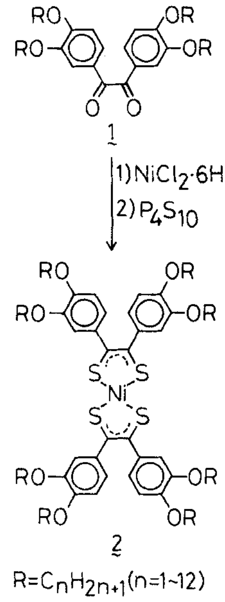
A series of disk-like complexes, bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dithiolene]nickel (abbreviated as $[(C_nO)_4DPD]_2Ni$, $n = 1 \sim 12$) have been synthesized in focusing our interest on the effect of the alkoxy chain length on the discotic mesomorphism. It was found that the $[(C_nO)_4DPD]_2Ni$ ($n = 2 \sim 4$) complexes have a monotropic discophase, and that the $[(C_nO)_4DPD]_2Ni$ ($n = 5 \sim 12$) complexes have an enantiotropic discophase (D_{hd}). The half-wave potentials for reduction of the $[(C_nO)_4DPD]_2Ni$ ($n = 1 \sim 12$) complexes are $-0.05 \sim -0.06$V (vs. SCE in dichloromethane solution). It is noteworthy that the π-acceptor discotic columnar liquid crystals can be obtained without impairment of the π-acceptor ability by introduction of the long alkoxy chains to the bis(dithiolene)nickel complex.

1. INTRODUCTION

We reported in a previous paper[1] on the synthesis and physical properties of the first π-acceptor discotic columnar liquid crystal, the bis[1,2-di(3′,4′-decyloxy-phenyl)ethane-1,2-dithiolene]nickel complex (Scheme I, $n = 10$).

In this report, we focus our interest on the effect of the alkoxy chain length on the discotic mesomorphism. A series of disk-like complexes, bis[1,2-(3′,4′-*n*-alkoxyphenyl)ethane-1,2-dithiolene]nickel (abbreviated as $[(C_nO)_4PDP]_2Ni$, $n = 1 \sim 12$), have been synthesized and the effects of the alkoxy chain length on discotic mesomorphism and their electrochemical properties have been investigated. We wish to describe here the mesomorphic properties and the electrochemistry of the $[(C_nO)_4DPD]_2Ni$ ($n = 1 \sim 12$) complexes.



SCHEME I Complexation of the benzils (1) with $NiCl_2 \cdot 6H_2O$ after treatment of P_4S_{10} in 1,4-dioxane.

TABLE I

Elemental analysis data, yields, melting points, and recrystallization solvents of the 3,3′,4,4′-tetraalkoxybenzil (1)

n	Elemental analysis(%) Found(Calcd.) C	H	Yield (%)	Melting point(°C)	Recrystallization solvent
1	65.46(65.45)	5.57(5.49)	23	224	Benzene
2	68.24(68.38)	6.76(6.78)	82	164	Ethanol
3	70.49(70.56)	7.63(7.74)	44	137	Ethanol
4	72.31(72.25)	8.47(8.49)	65	119,123	Ethanol
5	73.47(73.61)	9.05(9.09)	41	104,106	Ethanol
6	74.56(74.71)	9.48(9.57)	84	99	Ethanol
7	75.42(75.63)	9.86(9.97)	71	96	Ethanol
8	76.26(76.40)	10.28(10.32)	52	96	Ethanol
9	76.93(77.07)	10.60(10.61)	24	92	Ethyl Acetate
10	77.98(77.65)	10.88(10.86)	87	96	Ethyl Acetate
11	78.27(78.15)	11.10(11.08)	64	97	Ethyl Acetate
12	78.53(78.59)	11.26(11.28)	67	99	Ethyl Acetate

2. EXPERIMENTAL

2.1 Synthesis

The synthetic route of the present complexes, $[(C_nO)_4DPD]_2Ni$ (n = 1 ~ 12), is shown in Scheme I. The detailed procedures have been described in the previous paper.[1] In Table I are summarized the elemental analysis data, yields, melting points, and the recrystallization solvents for the precursor, 3,3′,4,4′-tetraalkoxybenzils (1). The benzils (1) for n = 4,5 have two melting points (double melting behavior). In Table II are summarized the elemental analysis data, yields, recrystallization solvents, and colors for the $[(C_nO)_4DPD]_2Ni$ (n = 1 ~ 12) complexes.

Measurements

The phase transition behaviors were observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82. The phase transition temperatures were measured with a differential scanning calorimeter, Rigaku TG-DSC. The X-ray diffraction measurements on the powder were performed with Cu-Kα radiation, using a Rigaku Geigerflex diffractometer equipped with a hand-made heating plate controlled by a thermoregulator.[3] The electrochemical property was determined in dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Cyclic voltammograms were obtained with a Yanagimoto Polarograic Analyzer P-900 and recorded with a Graphtec X-Y recorder WX1000. The measurements were made at a glassy-carbon working electrode vs. saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

It was found that the $[(C_nO)_4DPD]_2Ni$ (n = 2 ~ 4) complexes have a monotropic discophase, and that the $[(C_nO)_4DPD]_2Ni$ (n = 5 ~ 12) complexes have an enantiotropic discophase. The $[(C_1O)_4DPD]_2Ni$ complex doesn't exhibit a discophase and it decomposes at its melting point. The phase transition temperatures and enthalpy changes measured by a DSC and a polarizing microscope are summarized in Table III. In Table III, K* (K with superscript *) means that several unidentified transitions were observed in the crystalline phase. In the $[(C_8O)_4DPD]_2Ni$ complex, the $K^* \rightarrow D_{hd}$ transition occurs at 81°C in the case of the virgin sample, the $K \rightarrow D_{hd}$ transition occurs at 66°C in the case of the non-virgin sample. All transition temperatures of the complexes are plotted against the number of carbon atoms (n)

TABLE II

Elemental analysis data, yields, recrystallization solvents and colors of the bis(dithiolene)nickel complexes: $[(C_nO)_4DPD)_2Ni$ (n = 1 ~ 12).

n	Elemental analysis(%) Found(Calcd.) C	H	Yield (%)	Recrystallization solvent	Color
1	55.01(55.18)	4.74(4.63)	3.65	Ethyl Acetate	Black
2	58.74(58.99)	5.77(5.85)	36.2	Ethanol/Ethyl Acetate	Gray
3	62.01(61.96)	6.77(6.80)	14.0	Ethanol/Ethyl Acetate	Black
4	64.65(64.33)	7.60(7.56)	34.7	Ethanol/Ethyl Acetate	Grayish Blue
5	66.34(66.27)	8.19(8.18)	18.0	Ethanol	Loustrous green
6	67.91(67.88)	8.73(8.70)	42.1	2-Propanol	Loustrous green
7	69.48(69.25)	9.20(9.13)	29.3	2-Propanol	Dark green
8	70.41(70.42)	9.43(9.51)	34.0	2-Propanol	Black
9	71.46(71.44)	9.84(9.83)	7.41	2-Propanol	Black
10	72.40(72.32)	10.04(10.12)	41.0	Acetone/2-Propanol	Grayish Blue
11	73.09(73.11)	10.28(10.37)	28.1	Acetone/2-Propanol	Dark green
12	74.01(73.80)	10.49(10.59)	24.7	Acetone/2-Propanol	Dark green

TABLE III

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes (2).

n Phase $\xrightarrow{T_t\ (^\circ C)[\Delta H_t\ (kcal/mol)]}$ Phase^a

$\rightsquigarrow$ relaxation

1 $$\begin{tikzcd} K' \arrow[r, "261"] & \text{I.L. (decomposition)} \end{tikzcd}$$

2 $$\begin{tikzcd} K' \arrow[rr, "191"] & & \text{I.L.} \arrow[dl, "163"] \\ & D \arrow[ul, squiggly] & \end{tikzcd}$$

3 $$\begin{tikzcd} K' \arrow[rr, "159"] & & \text{I.L.} \arrow[dl, "131"] \\ & D \arrow[ul, squiggly] & \end{tikzcd}$$

4 $$\begin{tikzcd} K' \arrow[rr, "137"] & & \text{I.L.} \arrow[dl, "119"] \\ & D \arrow[ul, squiggly] & \end{tikzcd}$$

5 $$\begin{tikzcd} K' \arrow[r, shift left, "116"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "125[2.17]"] & \text{I.L.} \arrow[l, shift left] \end{tikzcd}$$

6 $$\begin{tikzcd} K' \arrow[r, shift left, "91"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "119[2.37]"] & \text{I.L.} \arrow[l, shift left] \end{tikzcd}$$

7 $$\begin{tikzcd} K' \arrow[r, shift left, "97"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "119[2.55]"] & \text{I.L.} \arrow[l, shift left] \end{tikzcd}$$

8 $$\begin{tikzcd} K' \arrow[r, shift left, "81"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "118[2.27]"] \arrow[dl, shift left, "66"] & \text{I.L.} \arrow[l, shift left] \\ K \arrow[ur, shift left] & & \end{tikzcd}$$

9 $$\begin{tikzcd} K' \arrow[r, shift left, "75[21.8]"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "118[2.56]"] & \text{I.L.} \arrow[l, shift left] \end{tikzcd}$$

TABLE III (*continued*)

10	$K \xrightleftharpoons{84[31.1]} D_{hd} \xrightleftharpoons{112[2.62]} I.L.$
11	$K^{*} \xrightleftharpoons{66} D_{hd} \xrightleftharpoons{111[2.47]} I.L.$
12	$K^{*} \xrightleftharpoons{72} D_{hd} \xrightleftharpoons{108[2.54]} I.L.$

[a] Phase nomenclature: K = crystal, D = discotic mesophase, Dhd = hexagonal disordered columnar mesophase, and I.L. = isotropic liquid.

* Unidentified phase transition were observed before melting to the mesophase or clearing to the isotropic liquid.

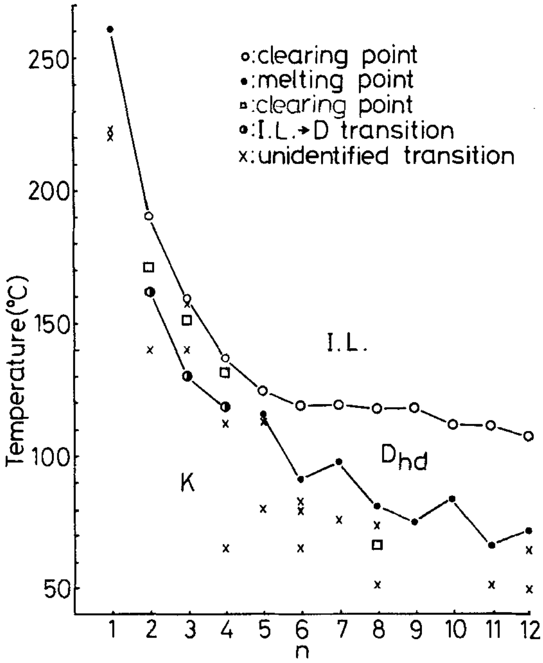


FIGURE 1 Phase transition temperatures vs. the number of carbon atoms(n) in the alkoxy chains.

in the alkoxy chains in Figure 1. In Figure 1, × marks denote the unidentified phase transitions in the crystalline phases.

3.1 Monotropic Mesomorphism of $[(C_nO)_4DPD]_2Ni$ ($n = 2 \sim 4$)

The$[(C_nO)_4DPD]_2Ni$ ($n = 2 \sim 4$) complexes have a monotropic discophase. When the $[(C_nO)_4DPD]_2Ni$ ($n = 2 \sim 4$) complexes are heated over the clearing points under the polarizing microscope and taken out from the hot plate and immediately put on to an aluminum plate at room temperature, a monotropic discophase is observed. As can be seen from Figure 2, the $[(C_nO)_4DPD]_2Ni$ ($n = 2,4$) complexes show the fan-shaped texture which is generally observed in D_{hd} mesophases.[4] The $[(C_3O)_4DPD]_2Ni$ complex shows a granular pattern. The relaxation from this monotropic discophase to the crystalline phase can be easily observed in the case of heating these monotropic discophases from room temperature at a heating rate of 10°C/min. The relaxation can occur in a little while even at room temerature. So, it is impossible to identify the discophase by X-ray diffraction measurements at room temperature. However, it is noteworthy that the $[(C_2O)_4DPD]_2Ni$ complex with very short side chains ($n = 2$) exhibits a discotic mesophase.

3.2 Enantiotropic Discotic Columnar Mesomorphism of $[(C_nO)_4DPD]_2Ni$ ($n = 5 \sim 12$)

The $[(C_nO)_4DPD]_2Ni$ ($n = 5 \sim 12$) complexes have an enantiotropic discophase. The same fan-shaped texture as the $[(C_nO)_4DPD]_2Ni$ ($n = 2,4$) complexes is observed for all the $[(C_nO)_4DPD]_2Ni$ ($n = 5 \sim 12$) complexes on cooling the isotropic liquid. Generally, this microscopic texture is characteristic of D_{hd} mesophases.[4]

The identification of these enantiotropic discophases was carried out by using X-ray diffraction measurements. Each X-ray diffraction pattern of the $[(C_nO)_4DPD]_2Ni$ ($n = 5, 6, 8, 10$ and 12) complexes in the mesomorphic temperature shows a diffuse band at $2\theta \simeq 20°$ ($d \simeq 4.4$ Å), which corresponds to the melting of the alkyl chains, and several narrow reflections which come from a two-dimensional hexagonal lattice (Table IV). Therefore, it could be assigned from these results that the $[(C_nO)_4DPD]_2Ni$ ($n = 5 \sim 12$) have a D_{hd} columnar mesophase. This assignment is consistent with the observed microscopic textures mentioned above. The lattice constants a of the two-dimensional hexagonal structures for the $[(C_nO)_4DPD]_2Ni$ ($n = 5, 6, 8, 10$ and 12) complexes are plotted against the number of the carbon atoms (n) in the alkoxy chains in Figure 3. A good linearity is observed between the lattice constant values and the number of the carbon atoms (n).

3.3 Electrochemistry

In Table V are summarized the half-wave potentials for the reduction of $[(C_nO)_4DPD]_2Ni$ ($n = 1 \sim 12$). As can be seen from Table V, the reduction potentials are nearly constant: these values are $-0.05 \sim -0.06$V vs. SCE in dichloromethane solution. There is no dependence of the reduction potentials on the alkoxy chain length. These potentials are somewhat less positive than the corresponding unsubstituted core complex, $NiS_4C_4Ph_4$.[5] However, we think that

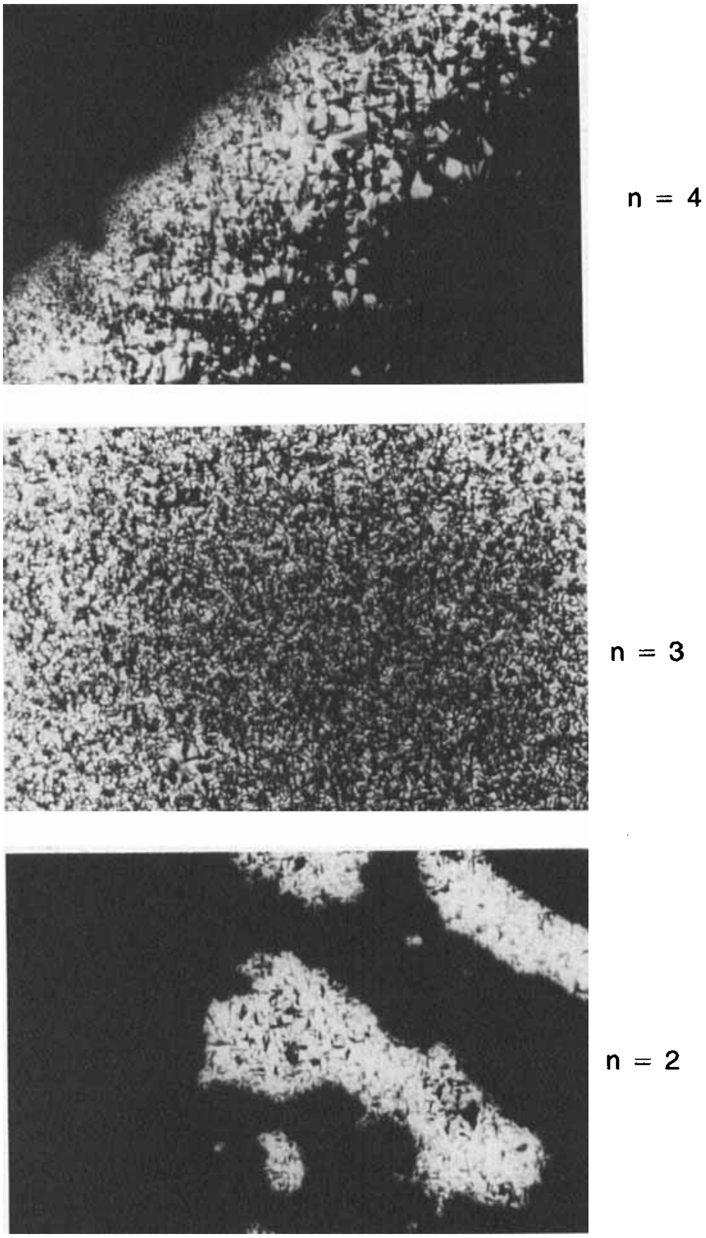


FIGURE 2 Photomicrographs of the monotropic discophase in the complexes (2) for $n = 2 \sim 4$ at room temperature.

the $[(C_nO)_4DPD]_2Ni$ ($n = 1 \sim 12$) complexes are fairly good π-acceptors, comparable to haloanils (chloranil, bromanil, and fluoranil).[6] Therefore, the discotic columnar liquid crystals can be obtained without impairment of the good π-acceptor ability by introduction of the long alkoxy chains.

TABLE IV

X-ray diffraction data of the bis(dithiolene)nickel complexes; $[(C_nO)_4DPD]_2Ni$.

n	Temperature (°C)	Spacing(Å)	Miller Indices	Lattice constant(Å)
5	115	22.1	(100)	a=25.2
		8.22	(210)	
		7.24	(300)	
6	105	22.9	(100)	a=26.4
		11.4	(200)	
		8.70	(210)	
		7.60	(300)	
8	100	25.6	(100)	a=29.5
		14.7	(110)	
		9.60	(210)	
10	89	28.2	(100)	a=32.7
		16.5	(110)	
		14.1	(200)	
12	80	31.0	(100)	a=35.6
		17.7	(110)	
		15.3	(200)	

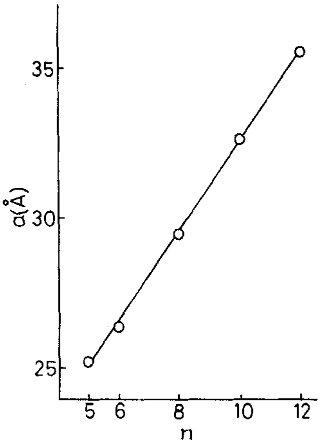


FIGURE 3 The lattice constants a(Å) of the D_{hd} mesophases of the complexes (2) vs. the number of the carbon atoms (n) in the alkoxy chains.

TABLE V

Cyclic voltammetric data obtained from bis(dithiolene)nickel complexes; $[(C_nO)_4DPD]_2Ni$ (n = 1 ~ 12).
Couple: $[(C_nO)_4DPD]_2Ni^0 + e^- \rightleftharpoons [(C_nO)_4DPD]_2Ni^{-1}$

n	Volts(vs. SCE in CH_2Cl_2)
0*	+0.03
1	-0.05
2	-0.05
3	-0.06
4	-0.05
5	-0.05
6	-0.06
7	-0.06
8	-0.06
9	-0.06
10	-0.06
11	-0.06
12	-0.06

* $NiS_4C_4Ph_4$.

4. CONCLUSION

Octaalkoxy-substituted bis(dithiolene)nickel complexes, bis[1,2-(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dithiolene]nickel (abbreviated as $[(C_nO)_4DPD]_2Ni$, n = 1 ~ 12), have been synthesized and characterized. It was found that the $[(C_nO)_4DPD]_2Ni$ (n = 2 ~ 4) complexes have a monotropic discophase, and that the $[(C_nO)_4DPD]_2Ni$ (n = 5 ~ 12) complexes have an enantiotropic discophase (D_{hd}). The half-wave potentials for reduction of the $[(C_nO)_4DPD]_2Ni$ (n = 1 ~ 12) complexes are nearly constant: these values are −0.05 ~ −0.06V vs. SCE in dichloromethane solution. It is noteworthy that the desired discotic columnar liquid crystals can be obtained without impairment of the good π-acceptor ability by introduction of the long alkoxy chains.

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