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Discotic Liquid Crystals of Transition Metal Complexes 13[1]: Synthesis and Discotic Columnar Mesomorphism of π-Donor Bis[1,2-di(3′,4′-di-n-alkoxyphenyl)ethane-1,2-dioximato]nickel(II) 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 13[1]: Synthesis and Discotic Columnar Mesomorphism of π-Donor Bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dioximato]nickel(II) 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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Disk-like complexes, bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dioximato]nickel(II) (abbreviated as $[(C_nO)_4DPG]_2Ni$, n = 4, 8, 12) have been synthesized and characterized. The $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes exhibit discotic hexagonal disordered columnar (D_{hd}) mesophases. Interestingly, it was found that the $[(C_8O)_4DPG]_2Ni$ complex has two kinds of D_{hd} mesophases. These complexes are the first discotic columnar liquid crystals in the bis(glyoximato)metal(II) system.

1. INTRODUCTION

A square planar d^8 complex bis[diphenylglyoximato]nickel(II) complex (abbreviated as $[DPG]_2Ni$) is stacked face to face forming a column perpendicular to the molecular plane.[2,3] Many studies of a one-dimensional conductor composed of the column of $[DPG]_2Ni$ as a donor and halogen as an acceptor have been reported.[3–7] Marks *et al.* reported that Iodination brings about an increase in conductivity of $>10^8$ along the column at room temperature. The effects of Iodination on such a drastic increase of conductivity are summarized as two points[3]: (1) partial oxidation (2) a decrease of the stacking distance within the column (ca. 0.27Å). On the other hand, since planar molecules pile up to form one-dimensional systems in discotic columnar mesophases, the following effects are expected: (i) alkyl chains of discogen create an apolar medium which allows the introduction of various organic dopants without perturbing the conducting chains,[8] (ii) a decrease of the stacking distance is caused by the introduction of the alkyl chains.[9,10] The first effect (i) allows to the use of various acceptor dopants besides halogen. The second effect (ii) causes the condition to obtain high conductivity. So, we intend to synthesize

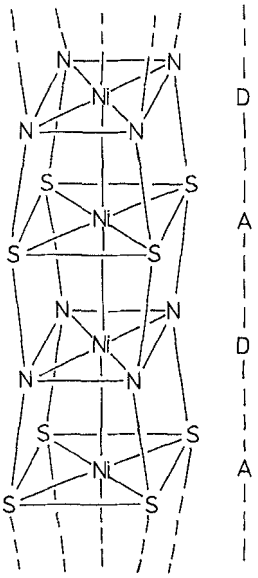
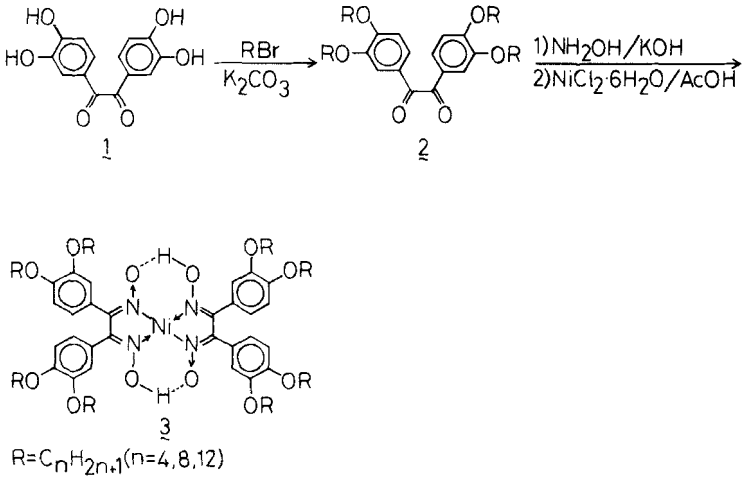


FIGURE 1 Schematic representation of the one-dimensional conductor composed of a Ni-Ni linear chain and four $(SN)_x$-like chains suggested by M. M.-Bélombé.[11]

a discotic columnar liquid crystal in the $[DPG]_2Ni$ system. If the discogen using the core of the $[DPG]_2Ni$ complex is synthesized, a new type of one-dimensional conductor suggested by Bélombé would be obtained.[11] The one-dimensional conductor consists of a linear chain with the central Ni atom surrounded by four parallel pseudo $(SN)_x$ chains (Figure 1).



SCHEME I Synthetic route of the octa-alkoxy-substituted bis(diphenylglyoximato)nickel(II) complexes (3).

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From this point of view, the octa-alkoxy chain-substituted $[DPG]_2Ni$ complex, bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dioximato]nickel(II) (abbreviated as $[(C_nO)_4DPG]_2Ni$, n = 4, 8, 12), has been synthesized by a new method developed by us in this work. As a result, it was found that the $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes exhibit discotic hexagonal disordered columnar (D_{hd}) mesophases. The $[(C_nO)_4DPG]_2Ni$ complexes (n = 4, 8, 12) are the first discotic columnar liquid crystals in the bis(glyoximato)metal(II)complex system. In this report, we describe the synthesis and the mesomorphic properties of the $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes.

2. EXPERIMENTAL

2.1 Synthesis

The synthetic route of the $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes (3) is shown in Scheme I. The precursors (1) and (2) were prepared by the method of Wenz.[12] The detailed procedures of the preparation of these precursors (1) and (2) were described in a previous paper.[13]

The $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes (3) were prepared by the reaction of the α-diketone derivative (2) and hydroxylamine hydrochloride in ethanol,[14] following the addition of an ethanol solution of nickel salt, and by neutralization. The detailed procedures are represented only for the $[(C_{12}O)_4DPG]_2Ni$ complex as follows, because the other complexes, $[(C_nO)_4DPG]_2Ni$ (n = 4, 8), could be synthesized in the same manner. In Table I are summarized the elemental analysis data, yields, reprecipitation (recrystallization) solvents, and colors of the $[(C_nO)_8DPG]_2Ni$ complexes (3).

2.2 Bis[1,2-di(3′,4′-di-*n*-dodecyloxyphenyl)ethane-1,2-dioximato]nickel(II) Complex (3), $[(C_{12}O)_4DPG]_2Ni$

To 150 ml of ethanol, hydroxylamine hydrochloride (6.00 g, 86.3 mmol) and 85% potassium hydroxide (6.00 g, 90.9 mmol) were added. The mixture was vigorously stirred for 15 min. and filtered to remove the precipitate. To the filtrate, 3,3′,4,4′-tetradodecyloxybenzil (2) (1.40 g, 1.48 mmol) was added. Under a nitrogen atmosphere, the mixture was refluxed with stirring for 12 h. To the hot reaction

TABLE I

Elemental analysis data, yields, reprecipitation (recrystallization) solvents, and colors of the $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes

n	Elemental analysis (%) Found(Calcd.) C	H	N	yield (%)	Reprecipitation (recrystallization) solvent	Color
4	65.17(64.69)	7.79(7.78)	5.12(5.03)	15	THF/Acetone	red
8	70.84(70.70)	9.96(9.67)	3.67(3.59)	15	THF/Acetone	red
12	73.82(74.03)	10.93(10.72)	2.89(2.79)	13	THF/Acetone	deep-red

mixture was added nickel(II) dichloride hexahydrate (0.15 g, 0.63 mmol) in 10 ml of ethanol. Then, reflux was continued for 30 min. more. The color of the reaction mixture turned to orange. The reaction mixture was cooled down to room temperature. It was basic at this stage. It was neutralized by glacial acetic acid. Red precipitate appeared with dropping glacial acetic acid. Neutralization was confirmed by pH test paper. The reaction mixture, including the red precipitate, was refluxed again for 2 h under the nitrogen atmosphere. It was cooled down to room temperature, 100 ml of water was added, and the whole mixture was filtered. The target compound was the red precipitate on the filter paper. The red precipitate was dissolved in chloroform and washed with water. The solvent was evaporated to give deep-red liquid crystals. The purification was carried out by column chromatography (silica gel, chloroform, Rf = 0.94) and reprecipitation (recyrstallization

TABLE II

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes (3)

n	T_t (°C)[ΔH_t (kcal/mol)] Phase → Phase[a]
4	K $\xrightarrow{249[5.81]}$ D_x $\xrightarrow{273[5.84]}$ I.L.[b] (D_{hd})
8	D_{hd1} $\xrightarrow{211[0.30]}$ D_{hd2} $\xrightarrow{232[6.40]}$ I.L.
12	D_{hd} $\xrightarrow{211[8.81]}$ I.L.

[a] Phase nomenclature: K=crystal, D_x=discotic mesophase which can be identified only by a polarizing microscope. D_{hd}=hexagonal disordered columnar mesophase, and I.L.=isotropic liquid.

[b] Gradual decomposition for heating-cooling cycles.

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(a) at r.t.

(b) at 208°C

(c) at 207°C

FIGURE 2 Photomicrographs of the $[(C_{12}O)_4DPG]_2Ni$ complex at various temperatures. See Color Plate IV.

for $n = 4$) by adding acetone into a hot solution of the product in tetrahydrofuran to give 0.19 mg of deep-red liquid crystals.
Yield 13%. ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 0.60 ~ 0.65 (m, 184H), 3.65 (t, J = 6Hz, 8H), 3.93(t, J = 6Hz, 8H), 6.63 ~ 6.90 (m, 12H) IR (neat, cm^{-1}), 2940, 2860, 1600, 1260.

2.3 Measurements

The synthesized products were identified by elemental analysis using a Perkin Elmer Elemental Analyzer 240B. The phase transition behaviors of these compounds were 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 measurements of the mesophases were performed using a Rigaku Geigerflex with Cu-Kα radiation equipped with a heating plate controlled by a thermoregulator.[15]

3. RESULTS AND DISCUSSION

It was found that the $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes exhibit discotic mesophases. The phase transition temperatures and enthalpy changes measured by the DSC and the polarizing microscope are summarized in Table II. The $[(C_nO)_4DPG]_2Ni$ (n = 8, 12) complexes have a columnar mesophase between room temperature and over 200°C. Only the $[(C_4O)_4DPG]_2Ni$ complex has a crystalline phase at room temperature.

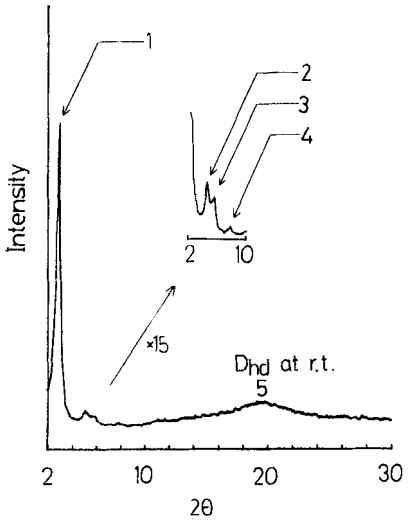

FIGURE 3 X-ray diffraction powder pattern of the $[(C_{12}O)_4DPG]_2Ni$ complex at r.t.

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3.1 Mesomorphic Properties of $[(C_{12}O)_4DPG]_2Ni$

This complex has a D_{hd} mesophase between room temperature and 211°C. The complex showed high viscosity with birefringence, and exhibited a deep-red color at room temperature (Figure 2(a)). When the complex was heated up from room temperature at a heating rate of 10°C/min., a spine texture appeared at ca. 200°C (Figure 2-b; at 208°C). On further heating, it cleared into an isotropic liquid at 211°C. When the isotropic liquid was cooled down at a cooling rate of −10°C/min., a fan-shaped texture appeared at 207°C (Figure 2-c). Generally, this texture is often observed in D_{hd} mesophases.[16] This texture remained until room temperature.

The X-ray powder diffraction pattern at room temperature is given in Figure 3. The pattern shows four narrow reflections, which are assigned to (100), (110), (200), and (210) in a two-dimensional hexagonal lattice. The lattice constant is 34.4Å. The pattern also gives a diffuse band at $2\theta \simeq 20°$ ($d \simeq 4.4$Å) which corresponds to the melt of the alkyl chains (Table III). Therefore, it could be deduced from these results that the phase is a discotic hexagonal disordered columnar (D_{hd}) mesophase. This assignment is consistent with the observation of the fan-shaped texture.

3.2 Mesomorphic Properties of $[(C_8O)_4DPG]_2Ni$

The $[(C_8O)_4DPG]_2Ni$ complex exhibits the same properties of mesomorphism, high viscosity with birefringence, and color as the $[(C_{12}O)_4DPG]_2Ni$ complex (Figure 4-a). When the complex was heated up from room temperature at a heating rate of 10°C/min., a spine texture appeared (Figure 4-b). On further heating, the texture became striated and another mesophase appeared at 211°C (Figure 4-c; at, 218°C). A small endothermic peak at 211°C in the DSC thermogram was also observed. The mesophase cleared into an isotropic liquid at 232°C. When the isotropic liquid was cooled down at a cooling rate of −10°C/min., a fan-shaped texture appeared at 226°C (Figure 4-d). On further cooling, the texture remained even at room temperature without distinctive change. However, the DSC thermogram of this non-virgin sample gave a small endothermic peak at 211°C again on the second heating run. It was reproducible in the DSC thermograms. Therefore, the $[(C_8O)_4DPG]_2Ni$ complex has two kinds of mesophases.

TABLE III

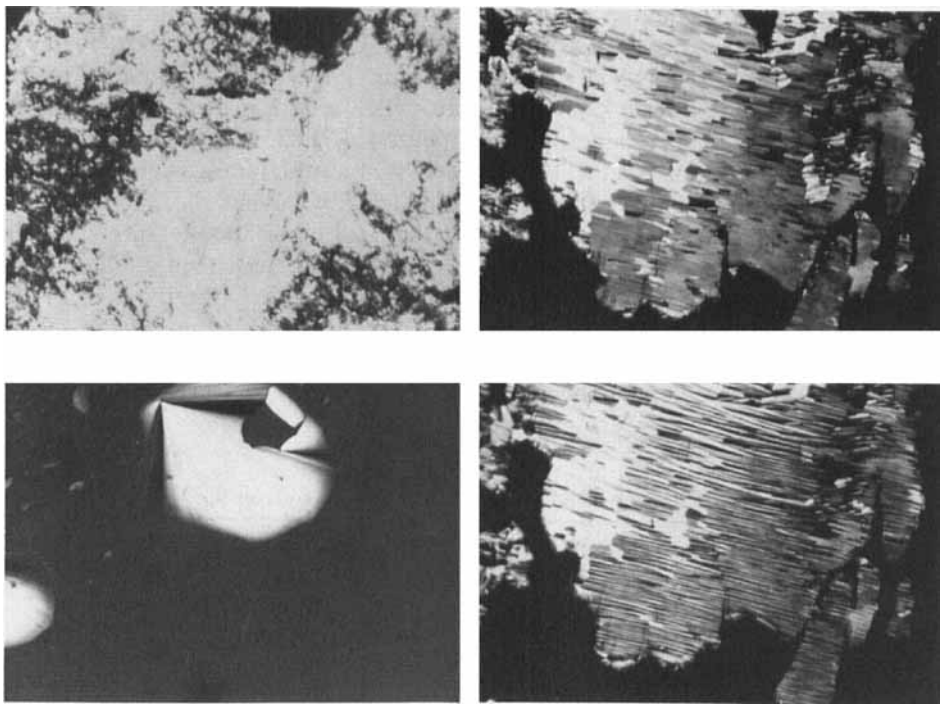
X-ray diffraction data of the $[(C_{12}O)_4DPG]_2Ni$ complex at r.t.

Peak No.	Spacing(Å) observed	calculated	Miller indices	Lattice constant
1	29.8	29.8	(100)	
2	17.1	17.2	(110)	a=34.4Å
3	14.9	14.9	(200)	
4	11.3	11.3	(210)	
5	≃4.4	-	*	

* The melt of alkyl chains

The X-ray powder analysis at room temperature and 215°C were performed to characterize these two mesophases. The pattern at room temperature gave seven narrow reflections (Figure 5). The pattern at 215°C gave nine narrow reflections (Figure 6). Both of the patterns also gave a diffuse band at d $\simeq$ 4.4Å ($2\theta \simeq 20°$, Peak No. 8 in Figure 5, Peak No. 10 in Figure 6). The narrow reflections observed in both of the patterns could be assigned to two-dimensional hexagonal lattices. Hence, both of these two mesophases could be assigned to D_{hd}. We defined here the lower temperature mesophase and the higher temperature mesophase as D_{hd1} and D_{hd2}, respectively. The lattice constant values of D_{hd1} an D_{hd2} are exactly the same (a = 29.6Å, Table IV). The X-ray measurements are not able to distinguish the difference between the mesophases D_{hd1} and D_{hd2}. This may be related to the small difference of the structures between them, which is compatible with the small enthalpy change at the transition D_{hd1}–D_{hd2} (0.30 kcal/mol).

The difference between D_{hd1} and D_{hd2} might be attributable to the difference between the degrees of the order in the column, because these phases give the same values for their lattice constants. Further studies are required, because it is the first discotic compound which exhibits two different hexagonal disordered columnar (D_{hd}) mesophases.



(c) at 218°C (d) at 226°C

FIGURE 4 Photomicrographs of the $[(C_8O)_4DPG]_2Ni$ complex at various temperatures. See Color Plate V.

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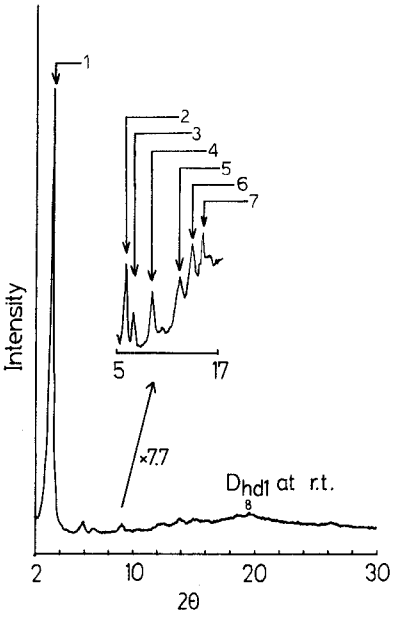

FIGURE 5 X-ray diffraction powder pattern of the $[(C_8O)_4DPG]_2Ni$ complex at r.t.

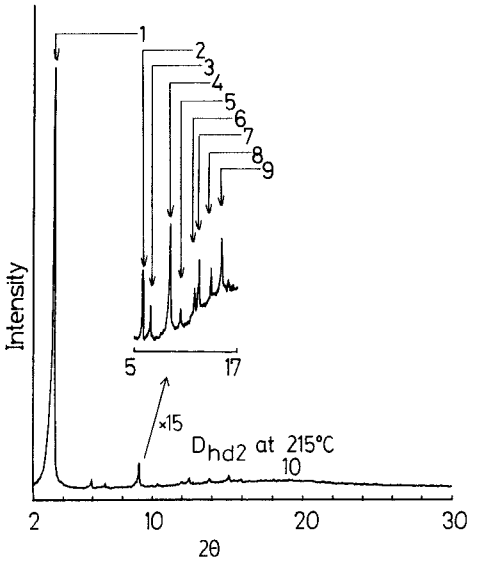

FIGURE 6 X-ray diffraction powder pattern of the $[(C_8O)_4DPG]_2Ni$ complex at 215°C.

3.3 Mesomorphic Properties of $[(C_4O)_4DPG]_2Ni$

The complex has needle-like crystals at room temperature (Figure 7-a). The natural texture obtained by cooling the sample from the isotropic liquid is a fan-shaped

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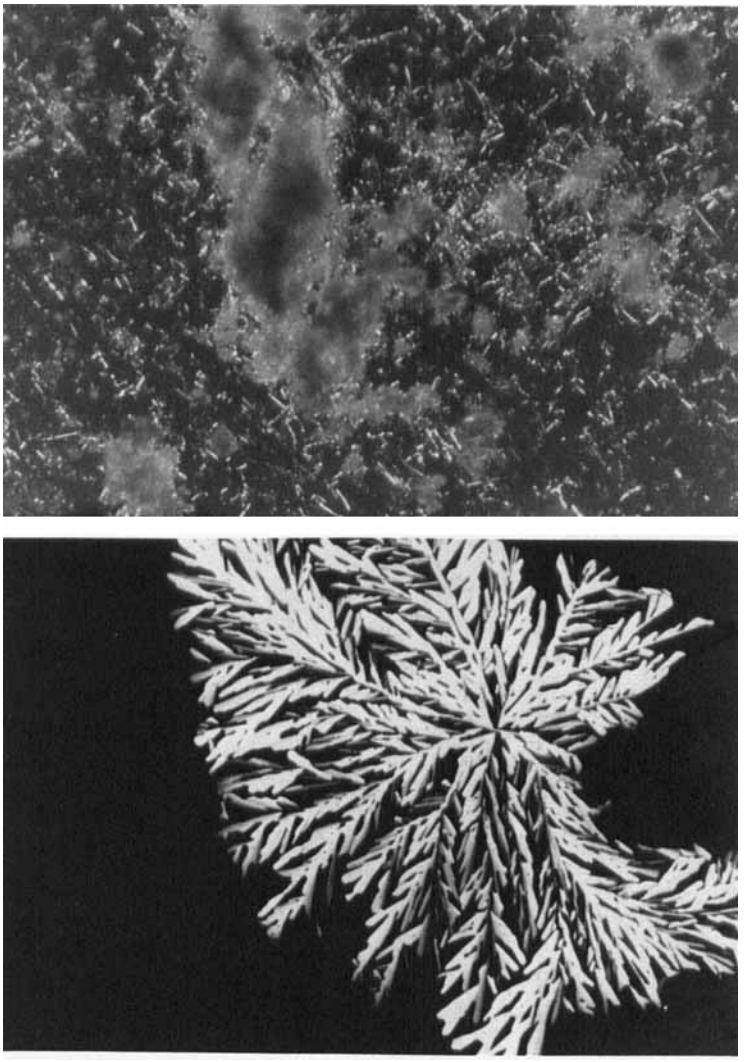

(a) at r.t.

(b) at 268°C

FIGURE 7 Photomicrographs of the $[(C_4O)_4DPG]_2Ni$ complex at various temperatures. See Color Plate VI.

texture (Figure 7-b), similar to the $[(C_nO)_4DPG]_2Ni$ (n = 8, 12) complexes. Therefore, it is suggested that the mesophase of the $[(C_4O)_4DPG]_2Ni$ complex is also a D_{hd} mesophase. However, the mesophase could not be characterized by X-ray measurements because of the temperature limit of the hot plate.

Thermochromism of these complexes was observed. The color of these complexes turns from red at room temperature to yellow at high temperature. This change is reversible and reproducible. The thermochromism phenomenon will be reported in a forthcoming paper.

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TABLE IV

X-ray diffraction data of the $[(C_8O)_4DPG]_2Ni$ complex at r.t. and 215°C

Temperature	Peak No.	Spacing(Å) observed	Spacing(Å) calculated	Miller indices	Lattice constant
r.t	1	25.7	25.7	(100)	a=29.6Å
	2	14.8	14.8	(110)	
	3	12.8	12.8	(200)	
	4	9.61	9.70	(210)	
	5	7.03	7.12	(310)	
	6	6.33	6.42	(400)	
	7	5.84	5.89	(320)	
	8	≃4.4	-	*	
215°C	1	25.7	25.7	(100)	a=29.6Å
	2	14.8	14.8	(110)	
	3	12.8	12.8	(200)	
	4	9.65	9.70	(210)	
	5	8.52	8.55	(300)	
	6	7.36	7.41	(220)	
	7	7.06	7.12	(310)	
	8	6.38	6.42	(400)	
	9	5.85	5.89	(320)	
	10	≃4.4	-	*	

* the melt of alkyl chains.

4. CONCLUSION

Bis[1,2-di(3′,4′-di-*n*-alkoxyphenyl)ethane-1,2-dioximato]nickel(II) (abbreviated as $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12)) complexes have been synthesized and characterized. The $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes exhibit D_{hd} mesophases. Interestingly, it was found that the $[(C_8O)_4DPG]_2Ni$ complex has two kinds of D_{hd} mesophase. The $[(C_nO)_4DPG]_2Ni$ (n = 4, 8, 12) complexes are the first discotic columnar liquid crystals in the bis(glyoximato)metal(II) system.

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