

Discotic liquid crystals of transition metal complexes 45[†]: parity effect of the number of d-electrons on stacking distances in the columnar mesophases of octakis-(*m*-alkoxyphenoxy)phthalocyaninato metal(II) complexes

Hiroyuki Sato^a, Kensaku Igarashi^a, Yoshitaka Yama^a, Masahiro Ichihara^a, Eiji Itoh^b and Kazuchika Ohta^{*a}

 ^a Smart Material Science and Technology, Department of Bioscience and Textile Technology, Interdisciplinary Graduate School of Science and Technology, Shinshu University, 1-15-1 Tokida, Ueda, 386-8567, Japan
 ^b Department of Electrical and Electronic Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

Received 22 April 2012 Accepted 5 June 2012

> **ABSTRACT:** We have synthesized 34 novel homologous discotic liquid crystals, octakis(*m*alkoxyphenoxy)phthalocyaninato metal(II) {abbreviated as $(m-C_0OPhO)_8PcM$ (M = Co(1), Ni(2), Cu(3), Zn(4) and $H_2(5)$; n = 8(a), 10(b), 12(c), 14(d), 16(e), 18(f) and 20(g)}, and investigated parity effect of the number of d-electrons on the stacking distances in their columnar mesophases. It was revealed from temperature-dependent wide angle X-ray diffraction studies that each of the cobalt(II) (d^7) complexes (1a-1g) and the copper(II) (d⁹) complexes (3b-3g) showed a single hexagonal ordered columnar (Col_{ho}) mesophase with a very short stacking distance at 3.3 Å, and that the nickel(II) (d^8) complexes (2a-2g) and the metal-free (d^0) derivatives (5a–5g) showed a single pseudo-hexagonal ordered columnar (Col_{tbo}) mesophase with a little bit longer stacking distances at 3.4 Å. Very interestingly, the nickel complex (2a) and metal-free derivatives (5a-5c) gave an extremely big (001) reflection peak with the second (002) reflection peak. Furthermore, the zinc(II) (d¹⁰) complexes (4a-4g) showed two different rectangular ordered columnar mesophases, $Col_{ro}(P2/m)$ and $Col_{ro}(P2_1/a)$, with a little bit longer stacking distance at 3.4 Å. Thus, the shorter stacking distance, 3.3 Å, appeared for the odd number of d-electrons, whereas the longer stacking distance, 3.4 Å, appeared for the even number of d-electrons. Hence, the stacking distances depend on parity of the number of d-electrons in the central metal(II). To our best knowledge, it is the first example of parity effect on the stacking distances in columnar mesophases.

> KEYWORDS: phthalocyanine, discotic liquid crystal, columnar liquid crystal, parity effect, metal complex.

INTRODUCTION

Since the first discotic liquid crystal was found by Chandrasekhar and his co-workers in 1977, many discotic liquid crystals have been synthesized for a great variety of central cores [1–7]. It is well-known that the π -conjugated central cores pile up face-to-face by the π – π interaction to form one-dimensional columns and exhibit columnar mesomorphism. Discotic liquid crystals can be applied to electronic devices, because charge carriers can move fast through their columns [8–12]. Fast charge carrier mobilities are favorable to the applications. Faster charge carrier mobilities could be obtained, if the intracolumnar stacking distance would become shorter in the ordered columns. As far as we know, a hexaazatriphenylene

^oSPP full member in good standing

^{*}Correspondence to: Kazuchika Ohta, email: ko52517@ shinshu-u.ac.jp, tel/fax: +81 (0)268-21-5492

[†]Part 44: Ariyoshi M, Sugibayashi-Kajita M, Suzuki-Ichihara A, Kato T, Kamei T, Itoh E and Ohta K. *J. Porphyrins Phthalocyanines*, in contribution

derivative gave the shortest stacking distance, 3.18 Å, in the ordered columnar mesophase and showed fast charge carrier mobility, 0.08 cm²/Vs [13]. For another example, a phthalocyanine double-decker lutetium complex, $[(C_{12}S)_8Pc]_2Lu$, showed very fast charge carrier mobilities, 0.36 cm²/Vs and 0.71 cm²/Vs, for the disordered and ordered columnar mesophases, respectively [10]. The faster mobility of 0.71 cm²/Vs is attributable to a very short stacking distance, 3.28 Å, in the ordered columnar mesophase.

Recently, we have synthesized six kinds of octakis (phenoxy)phthalocyaninato copper(II) derivatives: the derivatives substituted by one alkoxy chain at the ortho, meta or para position of the phenoxy group; the derivatives substituted by two alkoxy chains at the para/meta, meta/ meta or ortho/meta positions of the phenoxy group. We have systematically investigated the effect of substitution position of the alkoxy chains on their mesomorphism [14]. As a result, we found that the meta-positionsubstituted derivatives, $(m-C_nOPhO)_8PcCu$ (n = 12, 14), only gave a very short stacking distance at 3.33 Å in the Col_{bo} mesophase. The stacking distance appeared as a very strong and sharp reflection peak in the X-ray diffraction patterns. Therefore, in this work we have synthesized thirty-four novel meta-position-substituted homologous metal complexes, $(m-C_nOPhO)_8PcM$ {M = Co(1), Ni(2), Cu(3), Zn(4) and $H_2(5)$; n = 8(a), 10(b), 12(c), 14(d), 16(e), 18(f) and 20(g) to investigate the effect of central metal on their stacking distances.

It was revealed from temperature-dependent wide angle X-ray diffraction studies that the shorter stacking distance, 3.3 Å, appeared for the odd number of d-electrons, whereas the longer stacking distance, 3.4 Å, appeared for the even number of d-electrons. Hence, the stacking distances depend on parity of the number of d-electrons in the central metal(II). To our best knowledge, it is the first example of parity effect on the stacking distances in columnar mesophases. We wish to report here the interesting parity effect of the number of d-electrons on stacking distances in the columnar mesophases for octakis(*m*-alkoxyphenoxy)phthalocyaninato metal(II) complexes.

EXPERIMENTAL

Synthesis

We have synthesized a series of novel homologous metallomesogens, octakis(*m*-alkoxyphenoxy)phthalocyaninato metal(II) {abbreviated as $(m-C_nOPhO)_8PcM$ (M = Co(1), Ni(2), Cu(3), Zn(4) and H₂(5); n = 8(a), 10(b), 12(c), 14(d), 16(e), 18(f) and 20(g))}, following a synthetic route shown in Scheme 1. The precursors of the phenol derivatives (6) and the dicyano derivatives (7) were synthesized by our previously reported methods [14]. The phenol derivatives (6) could be prepared from commercially available chemicals, resorcinol

OH K₂CO₃, DMF K₂CO₃, DMA CN RBr NC RC ÔН ÓR 6 7 OR M = Co(1)Ni (2) Cu (3) Zn (4) H₂ (5) N (i), (ii), (iii), (iv), (v) $R = C_8 H_{17} (a)$ C₁₀H₂₁ (b) $C_{12}H_{25}$ (c) $C_{14}H_{29}$ (d) (i) 1-hexanol, DBU, CoCl₂·6H₂O (ii) 1-hexanol, DBU, NiCl₂ ÔR C₁₆H₃₃ (e) ÓR C₁₈H₃₇ (f) (iii) 1-hexanol, DBU, CoCl₂ C₂₀H₄₁ (g) 1-octanol, DBU, Zn(OAc)₂·2H₂O (iv) (v) 1-hexanol, DBU OR RO

Scheme 1. Synthetic route for $(m-C_nOPhO)_8PcM$: M = Co, H2, n = 8, 10, 12, 14, 16, 18 and 20. DMF = N, N-dimethylformamide, DMA = N, N-dimethylacetamide and DBU = 1, 8-diazabicyclo[5, 4, 0]-7-undecene

and bromoalkane (Wako). The dicyano derivatives (7) could be prepared from commercially available 4,5-dichlorophthalonitrile (Tokyo Kasei) and the phenol derivatives (6). The target phthalocyanine compounds $(m-C_nOPhO)_8PcM$ (1–5) could be synthesized from the dicyano derivatives (7). The detailed synthetic procedures are described below for the representative hexadecyloxy derivatives, $(m-C_{16}OPhO)_8PcM$ (M = Co, Ni, Cu, Zn and H₂; 1e, 2e, 3e, 4e and 5e).

3-hexadecyloxyphenol (6e). A mixture of resorcinol (2.00 g, 18.2 mmol), cetylbromide (5.50 g, 18.2 mmol), K_2CO_3 (5.00 g) and dry N,N-dimethylformamide (30 mL) was stirred at 100 °C for 3 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na₂SO₄ and evaporated in vacuum. The crude product was recrystallized from ethanol to remove the crystalline by-product, 1.3-dihexadecyloxybenzene. The precipitate was removed by filtration. The filtrate was evaporated in vacuum and purified by column chromatography (silica gel, CHCl₃, Rf = 0.30) to obtain 2.33 g of white power. Yield 38.3%, mp 63.9 °C. IR (KBr): v, cm⁻¹ 3451 (-OH), 2918 (-CH₂-). ¹H NMR (CDCl₃; TMS): δ, ppm 0.88 $(3H, t, J = 6.9 \text{ Hz}, -CH_3), 1.26 (24H, s, -CH_2CH_2CH_3),$ 1.40–1.47 (2H, m, -CH₂CH₂CH₃), 1.72–1.79 (2H, m, $-OCH_2CH_2$ -), 3.92 (2H, t, J = 6.7 Hz, $-OCH_2CH_2$ -), 6.40– 6.42 (2H, m, Ar-H), 6.47–6.49 (1H, m, Ar-H), 7.1 (1H, t, J = 8.5, Ar-H

4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (7e). A mixture of 3-hexadecyloxyphenol (6e) (1.87 g, 5.59 mmol), 4,5-dichloro-1,2-dicyanobenzene (0.50 g, 2.54 mmol), K₂CO₃ (5.00 g) and N,Ndimethylacetamide (14 mL) was stirred at 120 °C for 2 h. The reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na_2SO_4 and evaporated in vacuum. The residue was purified by column chromatography (silica gel, chloroform, Rf = 0.70) and recrystallization from ethanol to obtain 1.45 g of white powder. Yield 72.1%, mp 73.2 °C. IR (KBr): v, cm⁻¹ 2917, 2851 (-CH₂-), 2240 (-CN). ¹H NMR (CDCl₃; TMS): δ , ppm 0.88 (6H, t, J = 6.8 Hz, -CH₃), 1.26 (48H, s, -CH₂CH₂CH₃), 1.79 (4H, t, J = 7.4 Hz, $-OCH_2CH_2$ -), 3.94 (4H, t, J = 6.7 Hz, -OCH₂CH₂-), 6.60–6.64 (4H, m, Ar-O-Ar-H), 6.80–6.82 (2H, m, Ar-O-Ar-H), 7.20 (2H, m, Ar-O-Ar-H), 7.32 (2H, t, J = 8.2 Hz, CN-Ar-H).

2,3,9,10,16,17,23,24-octakis(3-hexadecyloxy-phe-noxy)phthalocyaninato cobalt(II) (1e). A mixture of 4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (**7e**) (0.200 g, 0.252 mmol), 1-hexanol (3 mL), DBU (8 drops) and CoCl₂· $6H_2O$ (6.31 mg, 2.65 × 10⁻² mmol) was refluxed for 16 h. The reaction mixture was poured into methanol to precipitate the target compound. The methanolic layer was removed by filtration and then the resulting precipitate was washed with ethanol, acetone and ethyl acetate, respectively. The residue was purified by recrystallization from ethyl acetate and then column

chromatography (silica gel, chloroform, Rf = 1.00) to obtain 0.102 g of green crystal. Yield 50.4%. MALDI-TOF mass data: see Table S1. UV-vis spectral data: see Table S2.

2,3,9,10,16,17,23,24-octakis(3-hexadecyloxy-phe-noxy)phthalocyaninato nickel(II) (2e). A mixture of 4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (**7e**) (0.491 g, 0.619 mmol), 1-hexanol (5 mL), DBU (2 drops) and NiCl₂ (20.0 mg, 1.55×10^{-1} mmol) was refluxed for 16h. The reaction mixture was poured into methanol to precipitate the target compound. The methanolic layer was removed by filtration and then the resulting precipitate was washed with ethanol, acetone and ethyl acetate, respectively. The residue was purified by recrystallization from ethyl acetate and then column chromatography (silica gel, chloroform, Rf = 1.00) to obtain 0.410 g of green crystal. Yield 82.1%. MALDI-TOF mass data: see Table S1. UV-vis spectral data: see Table S2.

2,3,9,10,16,17,23,24-octakis(3-hexadecyloxy-phe-noxy)phthalocyaninato copper(II) (3e). A mixture of 4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (**7e**) (0.250 g, 0.320 mmol), 1-hexanol (3 mL), DBU (8 drops) and CuCl₂ (15.0 mg, 0.850×10^{-1} mmol) was refluxed for 16 h. The reaction mixture was poured into methanol to precipitate the target compound. The methanolic layer was removed by filtration and then the resulting precipitate was washed with ethanol, acetone and ethyl acetate, respectively. The residue was purified by recrystallization from ethyl acetate and then column chromatography (silica gel, chloroform, Rf = 1.00) to obtain 86.4 mg of green crystal. Yield 33.4%. MALDI-TOF mass data: see Table S1. UV-vis spectral data: see Table S2.

2,3,9,10,16,17,23,24-octakis(3-hexadecyloxy-phe-noxy)phthalocyaninato zinc(II) (**4e**). A mixture of 4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (**7e**) (0.500 g, 0.634 mmol), 1-octanol (5 mL), DBU (4 drops) and Zn(OAc)₂·2H₂O (34.6 mg, 0.158 mmol) was refluxed for 24 h. The reaction mixture was poured into methanol to precipitate the target compound. The methanolic layer was removed by filtration and then the resulting precipitate was washed with ethanol and acetone, respectively. The collected solid was purified by solid-liquid extraction with acetone. The residue was further purified by column chromatography (silica gel, CHCl₃: tetrahydrofuran = 99:1, Rf = 0.55) to obtain 65.5 mg of green crystal. Yield 12.8%. MALDI-TOF mass data: see Table S1. UV-vis spectral data: see Table S2.

2,3,9,10,16,17,23,24-octakis(3-hexadecyloxy-phe-noxy)phthalocyanine (5e). A mixture of 4,5-bis(3-hexadecyloxyphenoxy)-1,2-dicyanobenzene (**7e**) (0.400 g, 0.505 mmol), 1-hexanol (5 mL) and DBU (4 drops) was refluxed for 24 h. The reaction mixture was poured into methanol to precipitate the target compound. The methanolic layer was removed by filtration and then the resulting precipitate was washed with ethanol, acetone

and ethyl acetate, respectively. The residue was purified by recrystallization from ethyl acetate and then column chromatography (silica gel, chloroform, Rf = 1.00) to obtain 0.213 g of green crystal. Yield 53.1%. MALDI-TOF mass data: see Table S1. UV-vis spectral data: see Table S2.

Measurements

The compounds synthesized here were identified with a ¹H NMR spectrometer (BRUKER Ultrashield 400 M Hz), an elemental analyzer (Perkin-Elmer elemental analyzer 2400) and a MALDI-TOF mass spectrometer (PerSeptive Biosystems Voyager DE-Pro). The elemental analysis data and MALDI-TOF mass spectral data were summarized in Table S1. Each of the electronic absorption spectra of all the phthalocyanine derivatives was recorded by using a HITACHI U-4100 spectrophotometer and summarized in Table S2. The phase transition temperatures and enthalpy changes were measured with a differential scanning calorimeter (Shimadzu DSC-50). Identification of the phases in these compounds was carried out by using a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage, and a wide angle X-ray diffractometer (Rigaku Rad) with Cu-K_{α} radiation equipped with a handmade hot stage [15]. Photomicrographs of the textures are shown in Fig. S1 for the representative derivatives, **1a**, **2a**, **3c**, **4a** and **5c**. Complete X-ray diffraction patterns are shown in Fig. S2 for the representative derivatives, **1d**, **2a**, **3c**, **4a** and **5c**. All the X-ray data are listed in Table S3.

RESULTS AND DISCUSSION

Phase transition behavior

Table 1 lists the phase transition behaviour of all the $(m-C_nOPhO)_8PcM$ (M = Co, Ni, Cu, Zn and H₂; n = $8\sim20$) derivatives together with the stacking distances in

Table 1. Phase transition temperatures and enthalpy changes of $(m-C_nOPhO)_8PcM$ {M = Co(1), Ni(2), Cu(3), Zn(4) and H₂(5); n = 8(a), 10(b), 12(c), 14(d), 16(e), 18(f) and 20(g)}

Complex	Stacking distance	Phase $T/^{\circ}C [\Delta H/(kJmol^{-1})]$ Phase ^a
<i>n</i> =8: 1a	3.30 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{hd} & \underbrace{191.2[56.2]}_{191.7[56.6]} & \text{I.L} \\ \hline \\ \text{Col}_{ho} & \underbrace{191.7[56.6]}_{\bullet} & \begin{array}{c} \\ \end{array} \end{array}$
<i>n</i> =10: 1b	3.30 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{\text{hd}} & \underbrace{187.0[29.0]}_{\text{1.L}} \\ & \underbrace{189.1[37.1]}_{\text{Col}_{\text{ho}}} \end{array}$
<i>n</i> =12: 1c	3.31 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{hd} & \xrightarrow{178.5[19.3]} \\ \hline 181.0[19.5] \\ \hline \end{array}$
<i>n</i> =14: 1d	3.31 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{hd} & \xrightarrow{179.9[32.7]} & \text{I.L} \\ & & 181.3[30.5] \\ \hline \\ & & & \\ \hline \end{array}$
<i>n</i> =16: 1e	3.35 Å [¶] (at 100 ^o C)	$\begin{array}{c} K_{1v} \xrightarrow{31.0[135]} & Col_{hd} & \underbrace{169.4[22.1]} & I.L \\ \hline K_{2} \xrightarrow{25.17[117]} & Col_{ho} & \underbrace{172.9[21.1]} & I.L \\ \end{array}$
<i>n</i> =18: 1f	3.36 Å [¶] (at 100 ºC)	$\begin{array}{c} K_{1v} \xrightarrow{38.3[165]} & \text{Col}_{hd} & \xrightarrow{154.0[10.8]} & \text{I.L} \\ \hline K_2 \xrightarrow{41.8[159]} & \text{Col}_{ho} & \xrightarrow{157.4[12.3]} & \hline \end{array}$
<i>n</i> =20: 1g	3.35 Å [¶] (at 100 °C)	$\begin{array}{ccc} K_{1v} & \underbrace{69.3[231]}_{\text{K}_{1v}} & Col_{\text{hd}} & \underbrace{157.0[10.7]}_{\text{I.L}} \\ K_{2} & \underbrace{53.5[188]}_{\text{Col}_{\text{ho}}} & Col_{\text{ho}} & \underbrace{157.5[10.9]}_{\text{Col}_{\text{ho}}} \end{array}$

(Continued)

Complex	Stacking distance	Phase —	T /ºC [∆ H /(kJmol ⁻¹)] → Phase ^a
<i>n</i> = 8: 2a <i>n</i> = 10: 2b	3.47Å [¶] (at r.t.) 3.43Å [¶] (at r.t.)	Co Co Co Co	$I_{rhd} (P2_{1/a}) \xrightarrow{173.0[22.5]} I.L$ $I_{rho} (P2_{1/a}) \xrightarrow{177.6[26.3]} \xrightarrow{1}$ $I_{rho} (P2_{1/a}) \xrightarrow{160.5[11.7]} I.L$ $I_{rho} (P2_{1/a}) \xrightarrow{162.9[16.0]} \xrightarrow{1}$
<i>n</i> = 12: 2c	3.51Å [¶] (at r.t.)	Co	I_{rhd} (P2 ₁ /a) 148.1[6.87] I.L I_{rho} (P2 ₁ /a) 149.1[11.5]
<i>n</i> = 14: 2d	3.47Å [¶] (at r.t.)	Co	I_{rhd} (P2 ₁ /a) 149.6[34.9] I.L 151.7[35.1]
<i>n</i> = 16: 2e	3.46Å [¶] (at 120 °C)	К 3 1.	$\xrightarrow{5[121.5]} (P2_{1/a}) \xrightarrow{146.5[9.22]} I.L$
<i>n</i> = 18: 2f	3.42Å [¶] (at 100 °C)	43.1 K –	$\xrightarrow{[175.9]} Col_{ho} \xrightarrow{139.1[11.6]} I.L$
n = 20: 2g	3.46Å [¶] (at 90 ⁰C)	39. K –	9[205.8] Col _{ho} 110.0[6.79]
<i>n</i> = 10: 3b	3.32 Å [¶] (at r.t.)	C	$\begin{array}{c} \text{DI}_{hd} & \underbrace{187.0[22.2]}_{\text{I.L.}} \\ 188.2[19.3] & \\ \hline \end{array}$
<i>n</i> = 12: 3c	3.33 Å [¶] (at r.t.)	C	$pl_{hd} \xrightarrow{178.4[27.4]} l.L.$ $pl_{ho} \xrightarrow{179.2[29.6]}$
<i>n</i> = 14: 3d	3.33 Å [¶] (at r.t.)	C	$bl_{hd} \xrightarrow{169.0[22.0]} l.L.$ $bl_{ho} \xrightarrow{169.6[25.5]} l.L.$
<i>n</i> = 16: 3e	3.36 Å [¶] (at 50 °C)	K 🚤 34.8	$5[64.8]$ \rightarrow Col _{ho} $\xrightarrow{160.9[18.0]}$ I.L.
<i>n</i> = 18: 3f	3.36 Å [¶] (at 90 ⁰C)	K 🚤 32.9	$\xrightarrow{\text{D[240]}} \text{Col}_{\text{ho}} \xrightarrow{152.3[27.8]} \text{I.L.}$
n = 20: 3g	3.35 Å [¶] (at 100 °C)	К 🗲 50.	$1[278] \longrightarrow \operatorname{Col}_{ho} \xrightarrow{156.3[20.6]} I.L.$

 Table 1. (Continued)

(Continued)

Complex	Stacking distance	T /ºC [∆ H /(kJmol ⁻¹)] Phase → Phase ^a
n = 8: 4a	3.45 Å [¶] (at 100 °C) 3.39 Å [¶]	$\begin{array}{c} \text{Col}_{rd} \\ (\text{P2/m}) \\ \hline \\ 132.6[2.88] \\ \hline \\ (\text{P2},ra) \\ \hline \\ \hline \\ (\text{P2},ra) \\ \hline \\ \hline \\ \hline \\ (\text{P2},ra) \\ \hline \\ \hline \\ \hline \\ \hline \\ (\text{P2},ra) \\ \hline \\ $
<i>n</i> = 10: 4b	(at 150 °C) 3.34 Å [¶] (at 60 °C) 3.35 Å [¶] (at 130 °C)	$\begin{array}{c} \text{Col}_{rd} \\ (\text{P2/m}) \end{array} \xrightarrow{118.9[4.45]} \\ \begin{array}{c} \text{Col}_{rd} \\ (\text{P2/m}) \end{array} \xrightarrow{118.9[5.40]} \\ \begin{array}{c} \text{Col}_{ro} \\ (\text{P2/m}) \end{array} \xrightarrow{120.9[5.40]} \\ \begin{array}{c} \text{Col}_{ro} \\ (\text{P2/m}) \end{array} \xrightarrow{162.4[11.9]} \\ \begin{array}{c} \text{I} \end{array}$
<i>n</i> = 12: 4c	3.39 Å [¶] (at 60 °C) 3.37 Å [¶] (at 130 °C)	$\begin{array}{c} \text{Col}_{rd} \\ (\text{P2/m}) & & \begin{array}{c} 103.2[3.00] \\ \hline (\text{P2/m}) & & \begin{array}{c} \text{Col}_{rd} \\ \hline (\text{P2/m}) & & \begin{array}{c} 175.5[11.6] \\ \hline (\text{P2/m}) & & \begin{array}{c} 105.3[4.74] \\ \hline (\text{P2/m}) & & \begin{array}{c} \text{Col}_{ro} \\ \hline (\text{P2/m}) & & \end{array} \end{array} \begin{array}{c} 176.6[14.5] \\ \hline (\text{P2/m}) & & \end{array} \end{array}$
<i>n</i> = 14: 4d	3.42 Å [¶] (at 70 °C) 3.36 Å [¶] (at 120 °C)	$\begin{array}{c} \text{Col}_{rd} \\ (\text{P2/m}) & \xrightarrow{99.1[3.73]} & \text{Col}_{rd} & \xrightarrow{166.5[23.8]} \\ \text{Col}_{ro} \\ (\text{P2/m}) & \xrightarrow{100.1[4.40]} & \text{Col}_{ro} & \xrightarrow{167.6[22.6]} \\ \hline & & & & \\ \text{(P2/m)} & & & \\ \hline \end{array}$
<i>n</i> = 16: 4e	3.43 Å [¶] (at 60 °C) 3.36 Å [¶] (at 100 °C)	$\begin{array}{c} K_{1v} \xrightarrow{35.1[141]} \operatorname{Col}_{rd} \xrightarrow{87.7[0.97]} \operatorname{Col}_{rd} \xrightarrow{122.6[3.32]} I.L \\ \overbrace{K_2} \xrightarrow{30.7[112]} \operatorname{Col}_{ro} \xrightarrow{85.4[3.93]} \operatorname{Co}_{ro} \xrightarrow{125.0[5.83] \bigstar} \\ \overbrace{(P2/m)} \xrightarrow{(P2/m)} \xrightarrow{(P2/m)} \operatorname{Col}_{ro} \xrightarrow{(P2/m)} \end{array}$
<i>n</i> = 18: 4f	3.40 Å [¶] (at 70 °C) 3.38 Å [¶] (at 110 °C)	$\begin{array}{c} K_{1v} \xrightarrow{47.4[142]} \underbrace{Col_{rd}}_{(P2/m)} \xrightarrow{90.1[3.21]}_{(P2_1/a)} \underbrace{\mathfrak{H}_{90}_{rd}}_{(P2_1/a)} \xrightarrow{149.0[9.95]}_{I.L.} \\ \underbrace{\mathfrak{S}_{2} \xrightarrow{39.6[148.8]}_{(P2/m)} \underbrace{\mathfrak{Sol}_{ro}}_{(P2/m)} \underbrace{\mathfrak{Sol}_{rd}}_{(P2_1/a)} \xrightarrow{\mathfrak{I}_{51.4[8.92]}}_{(P2_1/a)} \end{array}$
n = 20: 4g	3.41 Å [¶] (at 60 °C) 3.39 Å [¶] (at 120 °C)	$\begin{array}{c} \kappa_{1v} \xrightarrow{49.8[217]} \operatorname{Col}_{rd} \xrightarrow{90.4[3.51]} \operatorname{Col}_{rd} \xrightarrow{144.9[7.31]} I.L. \\ \overbrace{K_2} \xrightarrow{55.3[174]} \operatorname{Col}_{ro} \xrightarrow{89.8[4.40]} \operatorname{Col}_{ro} \xrightarrow{147.7[4.42]} \\ \overbrace{(P2/m)} \xrightarrow{(P2/m)} \xrightarrow{(P2/m)} \xrightarrow{(P2/m)} \end{array}$
n = 8: 5a	3.45 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{\text{rhd1}} & \underbrace{63.71[3.88]}_{(\text{P2}_{1}/\text{a})} & \underbrace{\text{Col}_{\text{rhd2}}}_{(\text{P2}_{1}/\text{a})} & \underbrace{177.1[29.4]}_{178.3[32.0]} & \downarrow \end{array} \right)$
<i>n</i> = 10: 5b	3.45 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{\text{rho}}(\text{P2}_{1}/\text{a}) & & \\ \hline & & \\ \text{Col}_{\text{rhd}}(\text{P2}_{1}/\text{a}) & & \\ \hline & & \\ \text{Col}_{\text{rho}}(\text{P2}_{1}/\text{a}) & & \\ \hline & & \\ \hline & & \\ \hline \end{array}$
n = 12: 5c	3.46 Å [¶] (at r.t.)	$\begin{array}{c} \text{Col}_{\text{rhd}}(\text{P2}_{1}/\text{a}) & \begin{array}{c} 158.5[31.7] \\ \hline \\ 161.6[34.2] \\ \hline \\ \text{Col}_{\text{rho}}(\text{P2}_{1}/\text{a}) \end{array} \end{array} \xrightarrow{1} 1$
<i>n</i> = 14: 5d	3.47 Å [¶] (at r.t.)	Col _{rhd} (P2 ₁ /a) 157.3[27.7] 158.5[29.8] ↓ 158.5[29.8]
<i>n</i> = 16: 5e	3.45 Å [¶] (at 100 ⁰C)	$\begin{array}{c} K_{1v} & \xrightarrow{26.6[139]} & \text{Col}_{\text{rhd}}(\text{P2}_{1}/\text{a}) & \xrightarrow{149.3[30.7]} & \text{I.L} \\ & \xrightarrow{31.4[133]} & \text{Col}_{\text{rho}}(\text{P2}_{1}/\text{a}) & \xrightarrow{150.3[30.9]} & & \\ \hline \end{array}$

Table 1. (Continued)

(Continued)

T /°C [Δ H /(kJmol⁻¹)] Complex Stacking Phase Phase^a distance 40.5[291] 143.5[31.7] 3.47 Å[¶] *n* = 18: **5f** K_{1v} - Col_{rhd}(P2₁/a) 11 (at 100 °C) 45.7[220] 145.0[37.5] Col_{rho}(P2₁/a) K₂ 73.6[314] 119.9[12.3] n = 20: 5g 3.46 Å[¶] Col_{rhd}(P2₁/a) (at 100 °C) 56.8[252] 124.9[12.7] Col_{rho}(P2₁/a) K_2

Table 1. (Continued)

the ordered columnar mesophases. As can be seen from this table, the $(m-C_nOPhO)_8PcCo$ (n = 8-14: 1a~1d) derivatives showed a hexagonal disordered columnar (Col_{bd}) mesophase for the freshly prepared (virgin) samples, whereas a hexagonal **ordered** columnar (Col_{ho}) mesophase appeared for the non-virgin samples when the isotropic liquid (I.L.) over the clearing point (c.p.) was cooled. For the much longer chain-substituted cobalt complexes (n = 16~20: 1e~1g), a crystalline (K_{1v}) phase appeared at lower temperatures and a Col_{hd} mesophase at higher temperatures for the virgin sample. When the I.L. over the c.p. was cooled, it gave an ordered columnar mesophase Col_{ho}, similarly to the shorter chain-substituted homologues $1a \sim 1d$. The stacking distances in the Col_{bo} mesophases of the cobalt complexes were very short and constant at 3.30–3.36 Å within the experimental error, irrespective of the alkoxy chain length.

 $(m-C_nOPhO)_8PcNi$ (n = 8-14: 2a~2d) The derivatives showed a pseudo-hexagonal disordered columnar $(Col_{rhd}(P2_1/a))$ mesophase for the virgin sample, and a pseudo-hexagonal ordered columnar $(Col_{rho}(P2_1/a))$ mesophase for the non-virgin sample on cooling from the I.L. To date, two kinds of pseudohexagonal mesophases, Col_{hr} and Col_{rh}, have been found. The Col_{hr} mesophase was found by Guillon et al. in 1991. In this mesophase, the whole molecules are packed in a 2D hexagonal symmetry, whereas the central core parts are packed in a rectangular symmetry [16]. On the other hand, the Col_{rh} mesophase was found by us in 2001. In this mesophase the whole molecules and the central core parts are oppositely packed in a rectangular symmetry and a 2D hexagonal symmetry, respectively [10]. These two pseudo-hexagonal mesophases give different stacking distances. The Col_{hr} mesophase shows a longer stacking distance at 4.0~5.0 Å similarly to conventional rectangular columnar mesophases, because this mesophase has a rectangular lattice for the core parts with a slipped stacking. On the other hand, the Col_{rh} mesophase shows a shorter stacking distance at 3.3~3.6 Å similarly conventional hexagonal columnar mesophases,

because this mesophase has a 2D hexagonal lattice for the core parts with a face-to-face stacking. Since the present pseudo-hexagonal mesophases of 2a~2e showed a shorter stacking distance at 3.43~3.51 Å, it could be identified as a Col_{rh} mesophase. The longer chain-substituted nickel derivatives (m-C_nOPhO)₈PcNi $(n = 16 \sim 20: 2e \sim 2g)$ gave a crystalline (K) phase at lower temperatures. The much longer chainsubstituted nickel derivatives, **2f** and **2g**, gave a Col_{ho} mesophase both for the virgin and non-virgin samples. The stacking distances of these Col_{ho} mesophases were 3.42~3.46 Å. Thus, the stacking distances in all the nickel derivatives 2a~2g are constant at 3.42~3.51 Å within the experimental error, irrespective of the chain length. Thus, the stacking distances of the nickel complexes are a little bit longer than those of the cobalt complexes.

The $(m-C_nOPhO)_8PcCu$ (n = 10~14: **3b~3d**) derivatives showed a disordered columnar mesophase Col_{hd} at rt for the virgin sample, and an ordered columnar mesophase Col_{ho} appeared when the I.L. over the c.p. was cooled. The longer chain-substituted derivatives, **3e~3g** (n = 16~20), showed a crystalline (K) phase at lower temperatures and an enatiotropic Col_{ho} mesophase at higher temperatures. The stacking distances of all the Col_{ho} mesophases are very short and constant at 3.32~3.36 Å within the experimental error.

The $(m-C_nOPhO)_8PcZn (n = 8~14: 4a~4d)$ exhibited a rectangular disordered columnar $(Col_{rd}(P2/m))$ mesophase at rt and transformed into another rectangular disordered columnar $(Col_{rd}(P2_1/a))$ mesophase on heating. When the I.L. over c.p. of the $Col_{rd}(P2_1/a)$ was cooled down, it gave the ordered columnar mesophases $Col_{ro}(P2_1/a)$ and then $Col_{ro}(P2/m)$. The much longer chain-substituted derivatives, 4e~4g (n = 16~20), showed a crystalline (K_{1v}) phase at lower temperatures and on heating it transformed into $Col_{rd}(P2/m)$ and then $Col_{rd}(P2_1/a)$ mesophases. When the I.L. over c.p. of the $Col_{rd}(P2_1/a)$ mesophases. When the I.L. over c.p. of the $Col_{rd}(P2_1/a)$ mesophases, when the Source context of the $Col_{rd}(P2_1/a)$ and $Col_{ro}(P2_1/a)$ and $Col_{ro}(P2_1/a)$ and $Col_{ro}(P2_1/a)$ and $Col_{ro}(P2_1/a)$ similarly to the shorter chain-substituted derivatives. All the stacking distances

of the $\text{Col}_{ro}(\text{P2/m})$ and $\text{Col}_{ro}(\text{P2}_1/\text{a})$ mesophases were constant at 3.34~3.45 Å and 3.35~3.39 Å, respectively.

The $(m-C_8OPhO)_8PcH_2$ (n = 8: 5a) derivatives showed two pseudo-hexagonal disordered columnar mesophases, $\operatorname{Col}_{rhd1}(P2_1/a)$ and $\operatorname{Col}_{rhd2}(P2_1/a)$ for the virgin sample. When the I.L. was cooled, it gave an ordered mesophase, $Col_{rho}(P2_1/a)$. For the longer chain-substituted derivatives of n = 10 - 14 (**5b**-**5d**), they gave a disordered columnar $Col_{thd}(P2_1/a)$ mesophase for the virgin sample and an ordered columnar Col_{rho}(P2₁/a) mesophase for the non-virgin sample. For the much longer chain-substituted derivatives of n =16~20 (5e~5g), the virgin sample gave a crystalline (K_{1v}) phase at rt and a disordered columnar $Col_{rhd}(P2_1/a)$ mesophase at higher temperatures. When the I.L. over the c.p. was cooled down, it gave an ordered columnar $\text{Col}_{\text{tho}}(\text{P2}_1/\text{a})$ mesophase and another crystalline (K₂) phase. The stacking distances of all the ordered columnar Col_{rho}(P2₁/a) mesophases were constant at 3.45~3.47 Å within the experimental error, irrespective of the chain length.

Therefore, the present meta-position-substituted homologs, $(m-C_nOPhO)_{s}PcM$ (M = Co, Ni, Cu, Zn and H_2), are categorized into two groups from the stacking distances. One group is the homologs of Co(II) (d⁷) and Cu(II) (d⁹) complexes showing a stacking distance at about 3.3 Å. Another group is the homologs of Ni(II) (d^8) , Zn(II) (d¹⁰), and H₂ (d⁰) derivatives showing a stacking distance at about 3.4 Å. The group of Co(II) and Cu(II) showing a very short stacking distance at 3.3 Å has odd number of the d electrons in the central metal(II) cation. On the other hand, the group of Ni(II), Zn(II) and H₂ showing a little bit longer stacking distance at 3.4 A has even number of the d electrons in the central part. It is very interesting that the stacking distances change with parity of the number of d electrons in the central metal(II) cation. The parity effect on the stacking distance may be originated from an additional magnetic Coulomb force. The metal(II) complexes of odd number of the d electrons in the central core may have an additional magnetic Coulomb force in the one-dimensional metal chain [17, 18]. Disk-like molecules are generally attracted by π - π interaction among the π -conjugated cores. For the metal(II) complexes having odd number of the d electrons in the central core, the magnetic Coulomb force among the cores may additionally attract the disks, which may shorten the stacking distances to 3.3 Å. On the contrary, the group of Ni(II), Zn(II) and H_2 showing a little bit longer stacking distance at 3.4 Å has even number of d electrons in the central part, so that these derivatives do not have such an additional magnetic Coulomb force.

Mesomorphic textures

As can be seen from the textures in Fig. S1, The mesophases of Col_{rho} , $\text{Col}_{ro}(\text{P2m})$ and $\text{Col}_{ro}(\text{P2}_1/\text{a})$ of the Ni, Zn and metal-free derivatives did not show homeotropic alignment. On the other hand, the Col_{ho} mesophases of the Co and Cu complexes showed

partially homeotropic alignment. When each of these Co and Cu complexes was cooled from the isotropic liquid, dark snow-flake-like dendrons having 6 hold symmetry appeared at first but on further developing they partially turned into bright dendrons. This indicated their homeotropic alignment was not perfect.

X-ray diffraction patterns

Figure 1 shows the X-ray diffraction patterns of $(m-C_{14}OPhO)_{s}PcM$ (M = Co, Ni, Cu, Zn and H₂: 1d, 2d, 3d, 4d and 5d) having the same chain length. In the left and right sides of this figure, the X-ray diffraction patterns of the virgin and non-virgin samples are shown, respectively. When the X-ray diffraction patterns are compared between them, it is apparent that the nonvirgin samples give a sharp and big (001) reflection peak corresponding to the stacking distance, but that the virgin samples give no peak due to the stacking distance. We think that it may be originated from regular aggregation of the discrete molecules on cooling from the I.L. phase. When the X-ray diffraction patterns of the non-virgin sample of M = Zn (4a) at 70 °C and 120 °C, the (001) reflection in Col_{ro}(P2/m) at 70 °C is small and broad but that of $\text{Col}_{ro}(\text{P2}_1/\text{a})$ at 120 °C is big and sharp.

In Fig. 2 are shown the (001) reflection peaks of the non-virgin samples of the (C_nOPhO)₈PcM derivatives for M = Co, Ni, Cu, Zn and H_2 ; n = 8 or 10 and 20 $\{(1a,1g)/(2a,2g)/(3b,3g)/(4a,4g)/(5a,5g)\}$ having two different chain lengths for the same central metal. In the left and right sides of this figure are shown the X-ray diffraction patterns for the shorter chain-substituted derivatives (n = 8 or 10) and the longest chainsubstituted derivatives (n = 20), respectively. As can be seen from this figure, the (001) reflection peaks of the shorter chain-substituted derivatives (n = 8 or 10) are much bigger than those of the longer chain-substituted derivatives (n = 20). The (001) reflection corresponds to the stacking distance of central cores, and the intensity may be weakened by thermal fluctuation of their peripheral chains. Accordingly, the longer the peripheral chains become, the smaller and broader the (001) reflection peak becomes with increasing the thermal fluctuation effect. On the contrary, the shorter the peripheral chains become, the bigger and sharper the (001) reflection peak becomes with decreasing the thermal fluctuation effect.

It is very noteworthy that $(m-C_8OPhO)_8PcNi$ (**2a**) and $(m-C_8OPhO)_8PcH_2$ (**5a**) gave an extremely big (001) reflection peak corresponding to the stacking distance. As can be seen from Fig. 3, the (001) reflection peaks of **2a** and **5a** are bigger than the normal one by about 10 times. Moreover, the second reflection (002) peak could be observed, which is the first example in columnar liquid crystals, so far as we know. Very interestingly, two additional small reflection (001) \pm d peaks, which are located at $h \pm d$ (h=3.47 Å, d=0.31 Å for **2a**; h=3.45



Fig. 1. X-ray diffraction patterns of $(m-C_{14}OPhO)_8PcM$. M = Co(1d), Ni(2d), Cu(3d), Zn(4d) and $H_2(5d)$



Fig. 2. X-ray diffraction patterns of $(m-C_nOPhO)_8PcM$. M = Co(1), Ni(2), Cu(3), Zn(4) and $H_2(5)$; n = 8(a) or 10(b) and 20(g)



Fig. 3. X-ray diffraction patterns of $(m-C_8OPhO)_8PcM$. M = Ni(2a) and $H_2(5a)$

Å, d = 0.30 Å for **5a**), could be also observed on the both sides of the big (001) reflection peak. These additional reflection (001) ± d peaks have never been reported in columnar liquid crystals. On the other hand, for the longer chain-substituted Ni complexes and metal-free derivatives, the (001) reflections could be observed as a small peak without the additional peaks. Thus, these two additional peaks could be observed only when the (001) reflection peak appears as an extremely big peak. Therefore, they may be related with unique stacking periodicity. They could not be fitted to any 3D reflections like (111), (101), (011) and so on. To date, there have been no other examples of additional (001) ± d reflection

peaks. Hence, further studies are necessary to reveal the origin.

CONCLUSION

We have synthesized a series of novel homologues octakis(*m*-alkoxyphenoxy)phthalocyaninato metal(II) complexes, $(m-C_nOPhO)_8PcM$ (M = Co(1), Ni(2), Cu(3), Zn(4) and H₂(5); n = 8(a), 10(b), 12(c), 14(d), 16(e), 18(f) and 20(g)). Their mesophases and stacking distances vary with the central metal(II). The Co(II) complexes (1a~1g) and Cu(II) complexes (3b~3g) show a Col_{ho} mesophase with a very short stacking distance at 3.3 Å. The Ni(II)

complexes $(2a \sim 2d)$ and the metal-free derivatives (5a - 5g) show a Col_{rho}(P2₁/a) mesophase with a little bit longer stacking distance at 3.4 Å. The Zn(II) complexes $(4a \sim 4g)$ show $Col_{ro}(P2/m)$ and $Col_{ro}(P2_1/a)$ mesophases with a little bit longer stacking distance at 3.4 Å. Thus, the stacking distances depend on parity of the number of d electrons in the central metal(II). To our best knowledge, it is the first example of parity effect on the stacking distances in columnar mesophases. Interestingly, the shorter the alkoxy chains become, the bigger and shaper the (001) reflection peak becomes. The (001) reflection peaks of the shorter chain-substituted $(m-C_{s}OPhO)_{s}PcNi$ (2a) and metal-free derivatives (5a-5c) are bigger than the normal (001) reflection peaks by about 10 times, and the second reflection (002) peaks could be also detected. They are the first examples of (002) peak in columnar liquid crystals, so far as we know.

Acknowledgements

This work is partially supported by Grant-in-Aid for science research (Grant No. 2236012311) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We are grateful to Associate Professor Mikio Yasutake, Saitama University for his kind measurements of TOF-MASS spectra of our compounds.

Supporting information

Tables S1–S3, Figs S1–S2 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

 Ohta K, Nguyen-Tran H-D, Tauchi L, Kanai Y, Megumi T and Takagi Y. In *Handbook of Porphyrin Science*, Vol. 12, Kadish KM, Smith KM and Guilard R. (Eds.), World Scientific Publishing: Singapore, 2011; Chapter 53, pp 1–120.

- 2. Kumar S. Chemistry of Discotic Liquid Crystals: From Monomers to Polymers, CRC Press; 2010.
- 3. Kumar S. Chem. Soc. Rev. 2006; 35: 83–109.
- Piechocki C, Simon J, Skoulios A, Guillion D and Weber P. J. Am. Chem. Soc. 1982; 104: 5245–5257.
- Raja KS, Ramakrishnan S and Raghunathan VA. Chem. Mater. 1997; 9: 1630–1637.
- 6. Bock H and Helfrich W. *Liq. Cryst.* 1992; **12**: 697–703.
- Herwing P, Kayser CW, Müllen K and Spie HW. Adv. Mater. 1996; 8: 510–513.
- Adam D, Schuhmacher P, Simmerer J, Haussling L, Siemensmeyer K, Etzbach KH, Ringsdorf H and Haarer D. *Nature* 1994; **371**: 141–143.
- Boden N, Bushby R J, Clements J and Monaghar B. *Phys. Rev. B* 1995; **52**: 13274–13279.
- Ban K, Nishizawa K, Ohta K, van de Craats AM, Warman JM, Yamamoto I and Shirai H. J. Mater. Chem. 2001; 11: 321–331.
- van de Craats AM, Stutzmann N, Bunk O, Nielsen MM, Watson M, Müllen K, Chanzy HD, Surringhaus H and Friend RH. *Adv. Mater.* 2003; 15: 495–499.
- Pisula W, Menon A, Stepputat M, Lieberwirth I, Kolb U, Tracz A, Sirringhaus H, Pakula T and Müllen K. *Adv. Mater.* 2005; 17: 684–689.
- Gearba RI, Lehmann M, Levin J, Ivanov DA, Koch MHJ, Barberá J, Debije MG, Piris J and Geerts YH. *Adv. Mater.* 2003; 15: 1614–1618.
- 14. Ichihara M, Suzuki A, Hatsusaka K and Ohta K. J. Porphyrins Phthalocyanines 2007; **11**: 503–512.
- Hasebe H. Master Thesis, Shinshu University, 1991; H. Ema. Master Thesis, Shinshu University, 1988.
- 16. Weber P, Guillon D and Skoulios A. *Liq. Cryst.* 1991; **9**: 369–382.
- Mukai H, Yokokawa M, Hatsusaka K and Ohta K. J. Porphyrins Phthalocyanines 2009; 13: 70–76.
- Mukai H, Hatusaka K and Ohta K. J. Porphyrins Phthalocyanines 2009; 13: 927–932.