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PAPER

# Flying-seed-like liquid crystals 2: unprecedented guidelines to obtain liquid crystalline compounds<sup>†</sup>

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In order to obtain novel "flying-seed-like" liquid crystals, we have prepared a series of bulky groupsubstituted phthalocyanine derivatives without any long alkyl chains: tetra[4-(triphenylmethyl)phenoxy]phthalocyaninato copper(II) (**1a**), tetra[4-(1,1-diphenylethyl)phenoxy]phthalocyaninato copper(II) (**1b**), tetra[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato copper(II) (**1c**), tetra[4-(*tert*-butyl)phenoxy]phthalocyaninato copper(II) (**1d**), and octa[4-(triphenylmethyl)phenoxy] phthalocyaninato copper(II) (**4**). We have established by using a polarizing optical microscope, a differential scanning calorimeter and a temperature-dependent small angle X-ray diffractometer that the Pc derivatives **1a–d**, but not 4, show columnar mesomorphism from r.t. to the extremely high decomposition temperatures at 450–500 °C. Their mesomorphism originates from thermal fluctuations due to free rotation of the bulky substituents. Thus, we have systematically demonstrated for the first time that liquid crystals can be also obtained by a series of novel bulky substituents instead of conventional long alkyl chains. Hence, we will be able to obtain a wide variety of new liquid crystalline compounds by using these bulky substituents instead of long alkyl chains. Very interestingly, these are unprecedented guidelines to obtain liquid crystalline compounds.

# Introduction

Since the first liquid crystal was found by Reinitzer in 1888,<sup>1</sup> about 101 000 liquid crystals<sup>2</sup> have been synthesized and investigated. Most of the liquid crystals are broadly categorized into "calamitic liquid crystals" of rod-like molecules as the first liquid crystalline group, and "discotic liquid crystals" of disk-like molecules as the second liquid crystalline group.3 These liquid crystalline materials are generally categorized by their molecular shapes, and each of them commonly has a flat lath-like or disklike core in the center and long alkyl chains in the periphery. When the material is heated, the long alkyl chains only melt to form soft parts and the central cores persistently do not melt. This leads to mesomorphism. Accordingly, people have long believed that mesomorphism is the result of "both the soft part of premelting long alkyl chains and the remaining solid part of central flat cores", for all the calamitic and discotic liquid crystals. However, it has been reported that a very few liquid crystals have neither peripheral long chains nor a central flat core.4-12

In 1911 Vorländer found mesomorphism of sodium diphenylacetate (Ph<sub>2</sub>CHCOONa) which has neither peripheral long alkyl

† Part 1: ref. 9 in this paper.



chains nor a central flat core, as shown in Fig. 1. However, the

mesomorphism of Ph<sub>2</sub>CHCOONa has been forgotten and not

been investigated for about 100 years.<sup>4</sup> It is attributable to the

molecular shape that is totally different from conventional

calamitic and discotic liquid crystals, and a very high mesophase

temperature region above 251 °C. There have been only a few

reports on this type of liquid crystalline metal carboxylates by

Demus et al.,<sup>5</sup> Sanesi et al.<sup>6,7</sup> and Binnemans et al.<sup>8</sup>



Fig. 1 Molecular structure and mesophase structure of the first flying-seed-like liquid crystal and a photograph of maple seeds.

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In 2006 we established by using temperature-dependent X-ray diffraction studies that  $Ph_2CHCOONa$  exhibits a hexagonal columnar (Col<sub>h</sub>) mesophase.<sup>9</sup> Since  $Ph_2CHCOONa$  resembles a flying seed as shown in Fig. 1, we named this type of liquid crystals as "flying-seed-like liquid crystals", which are the third liquid crystalline group.

Recently, Usol'tseva *et al.* reported a liquid crystalline phthalocyanine (Pc) derivative,  $(3Ph-PhO)_4PcCu$  (**1a** in Scheme 1), which has a central flat core and peripheral bulky triphenylmethylphenoxy groups instead of long alkyl chains.<sup>13,14</sup> This mesophase was identified as a Col<sub>h</sub> mesophase only from microscopic observations. The detailed mesophase structure has never been established by X-ray diffraction studies. However, the substituent triphenylmethylphenoxy group in this compound greatly resembles the diphenylmethyl group in the flying-seed-like liquid crystal of Ph<sub>2</sub>CHCOONa. Therefore, we regarded this phthalocyanine (Pc) derivative as one of the novel flying-seed-like liquid crystals.

In this work, we have synthesized a series of Pc derivatives including Usol'tseva's compound **1a** ((3Ph-PhO)<sub>4</sub>PcCu) and four novel Pc compounds (**1b–d** and **4**) substituted by a series of bulky groups, as illustrated in Schemes 1 and 2. As can be seen from these schemes, the Pc compounds, **1b** ((2Ph-PhO)<sub>4</sub>PcCu), **1c** ((1Ph-PhO)<sub>4</sub>PcCu) and **1d** ((0Ph-PhO)<sub>4</sub>PcCu), are substituted by four bulky groups of (1,1-diphenylethyl)phenoxy, (1-methyl-1-phenylethyl)phenoxy and (*tert*-butyl)phenoxy, respectively; the Pc compound **4** ((3Ph-PhO)<sub>8</sub>PcCu) is substituted by eight bulky



Scheme 1 Synthetic route for the Pc derivatives 1a–d. Abbreviation:  $(X-PhO)_y$ PcCu (X = the number of phenyl groups in substituent A, y = the number of A-PhO groups in the PcCu complex). DBU = 1,8-diazabicyclo [5,4,0]-undec-7-ene.



Scheme 2 Synthetic route for the Pc derivative 4, (3Ph-PhO)<sub>8</sub>PcCu.

groups of triphenylmethylphenoxy. We have established their mesomorphism in detail by using a polarizing optical microscope, a differential scanning calorimeter and a temperaturedependent small angle X-ray diffractometer. Surprisingly, the Pc derivatives 1a-d having four bulky groups showed columnar mesophases from r.t. to the extremely high decomposition temperatures at 450-500 °C; on the other hand, the Pc derivative 4 having eight bulky groups showed not a mesophase but a crystalline phase from r.t. to the decomposition temperature at about 470 °C. Thus, we have systematically demonstrated for the first time that liquid crystals can be also obtained by a series of novel bulky substituents instead of conventional long alkyl chains. Hence, we will be able to obtain a wide variety of new liquid crystalline compounds by using these bulky substituents instead of conventional long alkyl chains. Very interestingly, these are unprecedented guidelines to obtain liquid crystalline compounds. We wish to report here the interesting mesomorphism of 1a-d.

# Experimental

#### Synthesis

Scheme 1 shows the synthetic route for the tetra-substituted phthalocyanine derivatives **1a–d**. The starting material of 4-nitrophthalonitrile was purchased from Tokyo Chemical Industry (Tokyo Kasei). Dicyano derivatives **3a–d** were synthesized from 4-nitrophthalonitrile and the corresponding phenol derivatives **2a–d** by the method of Galanin *et al.*<sup>15</sup> The target phthalocyanine derivatives **1a–d** were synthesized from dicyano derivatives **3a–d** by using our previously reported microwave heating apparatus.<sup>16</sup> The synthetic route for the octa-substituted phthalocyanine derivative **4** is shown in Scheme 2. The starting material of 4,5-dichlorophthalonitrile was purchased from

Tokyo Chemical Industry (Tokyo Kasei). Dicyano derivative **5** was synthesized from 4,5-dichlorophthalonitrile and 4-(triphenylmethyl)phenol by the method of Wöhrle *et al.*<sup>17</sup> The target phthalocyanine derivative **4** was also synthesized from dicyano derivative **5** by using the microwave heating apparatus.<sup>16</sup> The detailed procedures are described as follows.

4-I4'-(Triphenvlmethvl)phenoxyl-1.2-dicvanobenzene (3a). Into a 50 ml three-neck flask, 4-nitrophthalonitrile (0.30 g, 1.7 mmol), dry N,N-dimethylformamide (6.0 ml), 4-(triphenylmethyl)phenol (0.70 g, 2.1 mmol) and anhydrous potassium carbonate (0.30 g, 2.3 mmol) were placed and the mixture was stirred at 110 °C under a nitrogen atmosphere for 2.5 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform,  $R_{\rm f} = 0.48$ ) twice to give 0.71 g of the white solid. Yield = 96%, m.p. = 228.2 °C. IR (KBr): 3050.90 (Ar-H), 2230.39 (-CN), 1593.60 (C=C), 1254.09 (ether) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>: TMS) δ 7.11–7.35 (m, 19H, Ar-H), 7.44 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 2.7$  Hz, CN-5-Ar-H), 7.85 (d, 1H, J = 3.0 Hz, CN-3-Ar-H), 8.11 (d, 1H, J = 8.8 Hz, CN-6-Ar-H).

Tetra[4-(triphenylmethyl)phenoxy]phthalocyaninato copper(II): (3Ph-PhO)<sub>4</sub>PcCu (1a). A mixture of 4-[4'-(triphenylmethyl) phenoxy]-1,2-dicyanobenzene (0.22 g, 0.48 mmol), CuCl<sub>2</sub> (0.032 g, 0.24 mmol), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (15 drops) and glycerin (8.0 ml) was poured into a test tube. The air in the test tube was replaced by a nitrogen atmosphere for 10 min. It was heated by microwave irradiation and kept at 200 °C for 20 min. After cooling to room temperature, water was added to the reaction mixture and filtered with suction. The residue was washed with methanol and ethanol. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_f = 1.0$ ) and purified from *n*-hexane by solid–liquid extraction twice to give 0.030 g of the dark blue glassy liquid crystal. Yield = 13%.

MALDI-TOF mass data: see Table 1. UV-vis spectral data: see Table 2.

**4-[4'-(1',1'-Diphenylethyl)phenoxy]-1,2-dicyanobenzene** (3b). Into a 50 ml three-neck flask, 4-nitrophthalonitrile (0.052 g, 0.30 mmol), dry N,N-dimethylformamide (1.0 ml), 4-(1,1-diphenylethyl)phenol (0.10 g, 0.36 mmol) and anhydrous potassium carbonate (0.059 g, 0.43 mmol) were placed and the mixture was stirred at 110 °C under a nitrogen atmosphere for 2.0 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed

with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_f = 0.76$ ) to give 0.12 g of the pale yellow solid. Yield = 97%, m.p. = 187.4 °C. IR (KBr): 3045.12 (Ar-H), 2979.27 (-CH<sub>3</sub>), 2221.95 (-CN), 1486.59 (C=C), 1239.63 (ether) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>: TMS)  $\delta$  2.16 (s, 3H, -CH<sub>3</sub>), 7.07–7.35 (m, 14H, Ar-H), 7.41 (dd, 1H,  $J_1 = 9.1$  Hz,  $J_2 = 2.7$  Hz, CN-5-Ar-H), 7.82 (d, 1H, J = 2.5 Hz, CN-3-Ar-H), 8.10 (d, 1H, J = 8.8 Hz, CN-6-Ar-H).

**Tetra[4-(1,1-diphenylethyl)phenoxy]phthalocyaninato copper(1): (2Ph-PhO)<sub>4</sub>PcCu (1b).** A mixture of 4-[4'-(1',1'-diphenylethyl)phenoxy]-1,2-dicyanobenzene (0.096 g, 0.24 mmol), CuCl<sub>2</sub> (0.032 g, 0.24 mmol), DBU (8 drops) and glycerin (6.0 ml) was poured into a test tube. The air in the test tube was replaced by a nitrogen atmosphere for 20 min. It was heated by microwave irradiation and kept at 200 °C for 20 min. After cooling to room temperature, water was added to the reaction mixture and filtered with suction. The residue was washed with methanol and ethanol. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_f = 1.0$ ) and purified from *n*-hexane by solid–liquid extraction twice to give 0.018 g of the dark blue glassy liquid crystal. Yield = 18%.

MALDI-TOF mass data: see Table 1.

UV-vis spectral data: see Table 2.

4-[4'-(1'-Methyl-1'-phenylethyl)phenoxy]-1,2-dicyanobenzene (3c). Into a 100 ml three-neck flask, 4-nitrophthalonitrile (1.0 g, 5.8 mmol), dry N,N-dimethylformamide (30 ml), 4-(1-methyl-1phenylethyl)phenol (1.9 g, 8.8 mmol) and anhydrous potassium carbonate (1.5 g, 11 mmol) were placed and the mixture was stirred at 110 °C under a nitrogen atmosphere for 2.5 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_{\rm f} = 0.63$ ) twice to give 1.9 g of the pale yellow solid. Yield = 95%, m.p. = 60.1 °C. IR (KBr): 3050.61 (Ar-H), 2970.06 (-CH<sub>3</sub>), 2231.87 (-CN), 1486.62 (C=C), 1250.44 (ether) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>: TMS) δ 1.67 (s, 6H, -CH<sub>3</sub>), 7.07-7.37 (m, 10H, Ar-H and CN-5-Ar-H), 7.77 (d, 1H, J = 2.3 Hz, CN-3-Ar-H), 8.09 (d, 1H, *J* = 8.8 Hz, CN-6-Ar-*H*).

Tetra[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato copper( $\mathbf{n}$ ): (1Ph-PhO)<sub>4</sub>PcCu (1c). A mixture of 4-[4'-(1'-methyl-1'phenylethyl)phenoxy]-1,2-dicyanobenzene (0.081 g, 0.24 mmol), CuCl<sub>2</sub> (0.032 g, 0.24 mmol), DBU (8 drops) and glycerin (6.0 ml) was poured into a test tube. The air in the test tube was replaced

Table 1 MALDI-TOF mass spectral data for the Pc derivatives 1a-d and 4

Derivative	Molecular formula	Molecular weight	Mass observed
1a: (3Ph-PhO)₄PcCu	C122H88O4N8Cu	1913.75	1915.99
1b: (2Ph-PhO) <sub>4</sub> PcCu	$C_{112}H_{s0}O_4N_8Cu$	1665.46	1665.46
1c: (1Ph-PhO) <sub>4</sub> PcCu	$C_{02}H_{72}O_4N_8Cu$	1417.18	1415.47
1d: (0Ph-PhO) PcCu	C <sub>72</sub> H <sub>c4</sub> O <sub>4</sub> N <sub>8</sub> Cu	1168.90	1167.40
4: $(3Ph-PhO)_8PcCu$	$C_{232}H_{160}O_8N_8Cu$	3251.42	3251.55

Table 2	UV-vis spectral	data in	chloroform	of the Pc	derivatives	1a-d and 4
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Derivative		$\lambda_{\max} (nm) (\log \varepsilon)$						
	Concentration <sup><i>a</i></sup> (×10 <sup>-5</sup> mol $l^{-1}$ )				Q-band			
		Soret-band			Q <sub>0-1</sub> band		$Q_{0-0}$ band	
1a: (3Ph-PhO) <sub>4</sub> PcCu	1.31	287.0 (4.74)	339.6 (4.86)	391.2 (4.41)	613.7 (4.61)		681.3 (5.17)	
1b: (2Ph-PhO) <sub>4</sub> PcCu	1.13	285.4 (4.86)	339.0 (4.97)	394.4 (4.47)	615.9 (4.75)		682.1 (5.28)	
1c: (1Ph-PhO) <sub>4</sub> PcCu	1.26	284.5 (4.73)	339.9 (4.82)	389.8 (4.35)	614.9 (4.60)		682.1 (5.15)	
1d: (0Ph-PhO) <sub>4</sub> PcCu	1.37	284.5 (4.60)	340.7 (4.70)	393.4 (4.26)	614.9 (4.47)		682.1 (5.01)	
4: (3Ph-PhO) <sub>8</sub> PcCu	1.20	289.3 (4.83)	341.6 (4.86)	398.8 (4.47)	613.7 (4.61)	650.9 (4.57)	682.3 (5.36)	
<sup><i>a</i></sup> In chloroform.								

by a nitrogen atmosphere for 20 min. It was heated by microwave irradiation and kept at 200 °C for 10 min. After cooling to room temperature, water was added to the reaction mixture and filtered with suction. The residue was washed with methanol and ethanol. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_{\rm f} = 1.0$ ) and purified from *n*-hexane by solid-liquid extraction twice to give 0.021 g of the dark blue liquid crystal. Yield = 25%.

MALDI-TOF mass data: see Table 1. UV-vis spectral data: see Table 2.

4-[4'-(tert-Butyl)phenoxy]-1,2-dicyanobenzene (3d). Into a 100 ml three-neck flask, 4-nitrophthalonitrile (1.5 g, 8.7 mmol), dry N,N-dimethylformamide (30 ml), 4-(tert-butyl)phenol (1.6 g, 10 mmol) and anhydrous potassium carbonate (1.7 g, 13 mmol) were placed and the mixture was stirred at 110 °C under a nitrogen atmosphere for 3.0 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_{\rm f} = 0.60$ ) to give 2.1 g of the pale yellow solid. Yield = 87%, m.p. = 115.7 °C. IR (KBr): 3078.05 (Ar-H), 2975.32 (-CH<sub>3</sub>), 2232.93 (-CN), 1503.05 (C=C), 1239.63 (ether) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>: TMS) δ 1.31 (s, 9H,  $-CH_3$ ), 7.10–7.15 (m, 2H, 3,5-Ar-*H*), 7.34 (dd, 1H,  $J_1 =$ 8.6 Hz, J<sub>2</sub> = 2.5 Hz, CN-5-Ar-H), 7.49 (m, 2H, 2,6-Ar-H), 7.76 (d, 1H, J = 2.5 Hz, CN-3-Ar-H), 8.08 (d, 1H, J = 8.8 Hz, CN-6-Ar-H).

Tetra[4-(tert-butyl)phenoxy]phthalocyaninato copper(II): (0Ph-PhO)<sub>4</sub>PcCu (1d). A mixture of 4-[4'-(tert-butyl)phenoxy]-1,2dicyanobenzene (0.066 g, 0.24 mmol), CuCl<sub>2</sub> (0.032 g, 0.24 mmol), DBU (8 drops) and glycerin (6.0 ml) was poured into a test tube. The air in the test tube was replaced by a nitrogen atmosphere for 20 min. It was heated by microwave irradiation and kept at 200 °C for 20 min. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was dispersed in acetone by using an ultrasonic washing machine (SHARP: UT-105S), and left for a while. The precipitate was collected by filtration and washed with acetone to give 0.045 g of the dark blue liquid crystal. Yield = 6.4%.

MALDI-TOF mass data: see Table 1. UV-vis spectral data: see Table 2.

Bis{4,5-[4'-(triphenylmethyl)phenoxy]}-1,2-dicyanobenzene (5). Into a 50 ml three-neck flask, 4-triphenylmethylphenol (1.1 g, 3.3 mmol), dry N,N-dimethylformamide (20 ml) and anhydrous potassium carbonate (3.5 g, 26 mmol) were placed and the mixture was stirred at 120 °C under a nitrogen atmosphere for 10 min. 4,5-Dichlorophthalonitrile (0.30 g, 1.5 mmol) was added to the mixture. The reaction mixture was stirred at 120 °C for a further 2.0 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. Then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform,  $R_{\rm f} = 0.75$ ) to give 1.1 g of the white solid. Yield = 96%, m.p. = 311.4 °C. IR (KBr): 3054.91 (Ar-H), 2228.88 (-CN), 1590.57 (C=C), 1228.57 (ether) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>: TMS)  $\delta$  6.88 (4H, d, J = 8.8Hz, -O-2,6-Ar-H) 7.08-7.29 (34H, m, -O-3,5-Ar-H and Ar-H), 7.94 (2H, s, CN-Ar-H).

Octa[4-(triphenylmethyl)phenoxy[phthalocyaninato copper(II): (3Ph-PhO)<sub>8</sub>PcCu (4). A mixture of bis{4,5-[4'-(triphenylmethyl) phenoxy]-1,2-dicyanobenzene (0.22 g, 0.28 mmol), CuCl<sub>2</sub> (0.018 g, 0.14 mmol), DBU (12 drops) and glycerin (8.0 ml) was poured into a test tube. The air in the test tube was replaced by a nitrogen atmosphere for 20 min. It was heated by microwave irradiation and kept at 200 °C for 30 min. After cooling to room temperature, water was added to the reaction mixture and filtered with suction. The residue was washed with methanol and ethanol. The crude product was purified by column chromatography (silica gel, dichloromethane,  $R_{\rm f} = 1.0$ ) and purified from *n*-hexane by solid-liquid extraction twice. Furthermore, the crude product was purified by column chromatography (silica gel, chloroform,  $R_{\rm f} = 0.95$ ) and purified from *n*-hexane by solid–liquid extraction twice to give 0.053 g of the green solid. Yield = 24%.

MALDI-TOF mass data: see Table 1.

UV-vis spectral data: see Table 2.

#### Measurements

The precursors of dicyanobenzene derivatives 3a-d and 5 were identified by <sup>1</sup>H-NMR measurement (BRUKER DRX-400) and FT-IR spectroscopy (Nicolet NEXUS 670). The phthalocyanine derivatives **1a-d** and **4** were identified by MALDI-TOF mass spectral measurement (PerSeptive Biosystems Voyager DE-Pro spectrometer) and UV-vis spectroscopy (HITACHI U-4100 spectrophotometer). MALDI-TOF mass spectral data and electronic spectral data of the phthalocyanine derivatives **1a-d** and **4** are summarized in Tables 1 and 2, respectively.

The phase transition sequences for the phthalocyanine derivatives **1a–d** and **4** were revealed by using a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a heating plate (Mettler FP82HT hot stage, Mettler FP-90 Central Processor) and a differential scanning calorimeter (Shimadzu DSC-50). The decomposition temperatures were measured by a Rigaku Thermo plus TG 820 thermogravity analyser. The identification of the mesophases was performed by using a small angle X-ray diffractometer (Bruker Mac SAXS System: Cu-K<sub> $\alpha$ </sub> radiation) equipped with a heating plate (Mettler FP82HT hot stage, Mettler FP-90 Central Processor). The measurement region was  $2\theta = 0.8-26.9^{\circ}$ .

## **Results and discussion**

#### Syntheses of the Pc derivatives 1a-d and 4

The target Pc derivatives **1a–d** and **4** were successfully synthesized by using microwave heating,<sup>16</sup> which causes rapid heating and accelerates the rate of reaction. Microwave heating enabled us to carry out the syntheses in a clean and energy-saving way.

Although elemental analyses of the Pc derivatives **1a–d** and **4** synthesised here were carried out, they were not completely burnt out so that the observed carbon content showed lower percentages than the calculated values by several percent. This is a well-known characteristic of less flammable phthalocyanine derivatives.<sup>18</sup> Hence, the results of the elemental analyses are not listed here. However, the MALDI-TOF mass and electronic spectral

Table 3 Phase transition sequences for the Pc derivatives 1a-d and 4

data listed in Tables 1 and 2 gave satisfactory evidence of successful syntheses of the target Pc compounds.

#### Phase transition sequences for the Pc derivatives 1a-d and 4

(3Ph-PhO)<sub>4</sub>PcCu (1a). As can be seen from Table 3, the freshly prepared (virgin) sample of (3Ph-PhO)<sub>4</sub>PcCu (1a) gave the same glass transition temperature  $(T_g)$  at 211 °C as reported by Usol'tseva *et al.*,<sup>13,14</sup> but the non-virgin sample showed another  $T_g$  at 183–187 °C lower than that of the virgin sample. On further heating, this derivative decomposed at *ca.* 500 °C. The reason why two  $T_g$  points were observed may be attributed to the following effects. The virgin sample was vitrified by evaporation of the solvent under reduced pressure on purification, whereas the non-virgin sample was vitrified by cooling the neat material in the Col<sub>h</sub> mesophase without solvent. The different cooling rates and viscosities may induce these two different  $T_g$  points.

Although Usol'tseva et al. observed the natural texture made by cooling from the isotropic liquid (I.L.) state,<sup>13,14</sup> we could observe neither the I.L. state nor the natural texture of (3Ph-PhO)<sub>4</sub>PcCu (1a). However, when it was pressed on the cover slip, it was rigid under the  $T_g$  points but sticky over the  $T_g$  points (Fig. 2a). Stickiness with birefringence is a characteristic of the general columnar liquid crystalline phase. The temperaturedependent small angle X-ray diffraction pattern of (3Ph-PhO)<sub>4</sub>PcCu at 375 °C is shown in Fig. 3a. As can be seen from this pattern, it gave both sharp and broad peaks characteristic of the liquid crystalline phase. The sharp peaks 1-4 could be assigned to the reflections from a 2D hexagonal lattice (a = 30.0 Å). Broad peaks, #1 (no. 5) and #2 (no. 6), are attributable to the average distances among the freely rotating phenoxy groups and triphenylmethyl groups, respectively. As can be seen from the XRD patterns in Fig. 3a-e, each of the

Derivative	Р	hase <u>T(°(</u>	C) [∆H(kJ	/mol)]	Phase <sup>a</sup>	
	T T	¯ <sub>g</sub> = 211 (virgin ¯ <sub>g</sub> = 183∼187 (n	) on-virgin)	)	<i>ca.</i> 500	
1a : (3Ph-PhO)₄PcCu	Glassy Col <sub>ho</sub>	<ul> <li>▼</li> <li>− 1261</li> </ul>	21	Col <sub>ho</sub>		decomp.
1b : (2Ph-PhO) <sub>4</sub> PcCu	Glassy Col <sub>ho</sub>	1 <sub>g</sub> − 120~	<u>→</u>	Col <sub>ho</sub>	<i>ca.</i> 450 ►	decomp.
1c : (1Ph-PhO)₄PcCu	Col <sub>ho1</sub>	76.5 [1.10	)] ►	Col <sub>ho2</sub>	<i>ca.</i> 480 ───►	decomp.
1d : (0Ph-PhO)₄PcCu	Col <sub>rho</sub>		ca.	500		decomp.
4 : (3Ph-PhO) <sub>8</sub> PcCu	К		ca.	470		decomp.

<sup>a</sup> Phase nomenclature: Col<sub>ho</sub> = hexagonal ordered columnar mesophase, Col<sub>rho</sub> = pseudo-hexagonal ordered columnar mesophase, K = crystal.



**Fig. 2** Photomicrographs of the Pc derivatives **1a–d** and **4**. (a) **1a**: (3Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho</sub> at 375 °C; (b) **1b**: (2Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho</sub> at 375 °C; (c) **1c**: (1Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho1</sub> at r.t.; (d) **1c**: (1Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho2</sub> at 375 °C; (e) **1d**: (0Ph-PhO)<sub>8</sub>PcCu; Col<sub>rho</sub> at 375 °C; and (f) **4**: (3Ph-PhO)<sub>8</sub>PcCu; K at 375 °C.



**Fig. 3** X-Ray diffraction patterns of the Pc derivatives **1a–d** and **4**. (a) **1a**: (3Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho</sub> at 375 °C; (b) **1b**: (2Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho</sub> at 375 °C; (c) **1c**: (1Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho1</sub> at r.t.; (d) **1c**: (1Ph-PhO)<sub>4</sub>PcCu; Col<sub>ho2</sub> at 375 °C; (e) **1d**: (0Ph-PhO)<sub>8</sub>PcCu; Col<sub>rho</sub> at 375 °C; and (f) **4**: (3Ph-PhO)<sub>8</sub>PcCu; K at 375 °C.

tetra-substituted Pc derivatives **1a–d** gave a broad peak #1 in a region of  $2\theta = 10-15^{\circ}$ , so it may correspond to a common structure of the phenoxy parts in these derivatives **1a–d**. On the other hand, another broad peak #2 at  $2\theta \approx 20^{\circ}$  could be observed only for **1a**, so it may correspond to the triphenylmethyl parts. These broad peaks represent thermal fluctuations of the bulky substituents, which can cause the softness necessary for the liquid crystalline phase. This means that liquid crystals can be also obtained by thermal fluctuation of a series of novel bulky substituents instead of conventional long alkyl chains. Peak 7 in the high angle region could be assigned to a stacking distance (= intracolumnar molecular distance: h = 3.58 Å). In Table 4 these X-ray data are listed.

Thus, it was established from the XRD study that (3Ph-PhO)<sub>4</sub>PcCu (1a) shows a Col<sub>ho</sub> mesophase, which is consistent with the identification from polarizing microscopic observation by Usol'tseva *et al.*<sup>13,14</sup>

(2Ph-PhO)<sub>4</sub>PcCu (1b). As can be seen from Table 3, (2Ph-PhO)<sub>4</sub>PcCu (1b) showed a  $T_g$  point at 126–131 °C and decomposed at *ca.* 450 °C. This derivative 1b gave neither I.L. nor the natural texture, and neither did 1a. When 1b was pressed on the cover slip over the  $T_g$  point, it showed stickiness with birefringence (Fig. 2b). Therefore, 1b apparently showed mesomorphism. The temperature-dependent small angle X-ray diffraction pattern of 1b gave both sharp and broad peaks (Fig. 3b) which are characteristic of mesomorphism. The sharp peaks 1–4 could be assigned as the reflections from a 2D hexagonal lattice (a = 29.6 Å). The broad peak #1 (no. 5) may correspond to the average distance among the freely rotating phenoxy parts. Peak 6 in the high angle region could be assigned to a stacking distance (h = 3.49 Å). From these X-ray data, the mesophase of (2Ph-PhO)<sub>4</sub>PcCu (1b) could be identified as a Col<sub>ho</sub> mesophase.

(1Ph-PhO)<sub>4</sub>PcCu (1c). As can be seen from Table 3, (1Ph-PhO)<sub>4</sub>PcCu (1c) showed no  $T_g$  point unlike 1a and 1b, but two different Colho mesophases: Colho1 from r.t. to 76.5 °C and Colho2 from 76.5 °C to the decomposition temperature at ca. 480 °C. This derivative 1c also gave neither I.L. nor the natural texture, and neither did 1a and 1b. When 1c was pressed on the cover slip at r.t., it showed softness with birefringence and spread like boiled Japonica rice (Fig. 2c). On further heating, it became much softer to form a thinner film by pressing (Fig. 2d). Therefore, 1c showed mesomorphism from r.t. Each of the temperature-dependent small angle X-ray diffraction patterns of 1c at r.t. and 375 °C gave both sharp and broad peaks (Fig. 3c and d) which are characteristic of mesomorphism. The sharp peaks 1-4 in Fig. 3c could be assigned as the reflections of a 2D hexagonal lattice having a = 26.6 A. The broad peak #1 (no. 5) may correspond to the average distance among the freely rotating phenoxy parts. Peak 6 in the high angle region could be assigned to a stacking distance (h = 3.35 A). In the same manner, the diffraction peaks in Fig. 3d could be analysed to obtain the lattice constants, a = 28.1 A and h = 3.46 A for Col<sub>ho2</sub> at 375 °C. Thus, the mesophases of (1Ph-PhO)<sub>4</sub>PcCu (1c) could be identified as two different Colho mesophases.

(0Ph-PhO)<sub>4</sub>PcCu (1d). As can be seen from Table 3, (0Ph-PhO)<sub>4</sub>PcCu (1d) showed a single mesophase from r.t. to the

#### Table 4 X-Ray data for the Pc derivatives 1a-d<sup>a</sup>

Derivative (mesophase)	Lattice constants/Å	Peak no.	Spacing/Å		
			Observed	Calculated	Miller indices $(h \ k \ l)$
<b>1a</b> : (3Ph-PhO) <sub>4</sub> PcCu (Col <sub>ho</sub> at 375 °C)	$a = 30.0, h = 3.58, Z = 1.0$ for $\rho = 1.0$	1	26.0	26.0	$(1\ 0\ 0)$
· · · · · · · · · · · · · · · · · · ·		2	15.1	15.0	$(1 \ 1 \ 0)$
		3	13.0	13.0	$(2\ 0\ 0)$
		4	9.79	9.82	$(2\ 1\ 0)$
		5	ca. 6.9		#1
		6	ca. 4.7		#2
		7	3.58		$(0\ 0\ 1)^h$
<b>1b</b> : (2Ph-PhO) <sub>4</sub> PcCu (Col <sub>bo</sub> at 375 °C)	$a = 29.6, h = 3.49, Z = 1.0$ for $\rho = 1.0$	1	25.7	25.7	$\dot{1}$ 0 $\dot{0}$
		2	14 7	14.8	(110)
		3	12.6	12.8	(2,0,0)
		4	9.60	9 70	(2 1 0)
		5	ca 65		(2 I 0) #1
		6	3 49		$(0, 0, 1)^h$
1e: (1Ph-PhO), PcCu (Column at r t)	$a = 26.6, h = 3.35, Z = 1.0$ for $\rho = 1.0$	1	23.0	23.0	(100)
		2	12.8	13.3	$(1 \ 0 \ 0)$
		3	11.1	11.5	(200)
		4	8 50	8 69	$(2 \ 0 \ 0)$
		5	ca 57	0.09	(210) #1
		6	3 35		$(0, 0, 1)^h$
1e: (1Ph PhO), PcCu (Col at 375 °C)	a = 281 $h = 3.46$ $Z = 1.0$ for $a = 1.0$	1	24.3	24.3	(0 0 1)
I.e. $(1711-7110)_4$ recu $(Col_{ho2}$ at 575 C)	u = 26.1, n = 5.40, Z = 1.0101 p = 1.0	2	12.9	12.9	$(1 \ 0 \ 0)$
		2	13.0	13.0	(110)
		3	11.0	11.0	(2 0 0)
		4	0.95	0.9	(210)
		5	246	3	#1
14. (0Ph PhO) P-C (C-1	- 44.4 h 25.0 h 2.44.7 2.0 f-r	0	3.40		$(001)^{n}$
Id: $(0Ph-PhO)_4PcCu$ (Col <sub>rho</sub> at 3/5 °C)	a = 44.4, b = 25.0, n = 3.44, Z = 2.0 for	1	16.1	16.6	(2 0 0), (1 1 0)
	ho = 1.0	2	10.1	10.0	(2 1 0)
		3	12.0	12.5	(0 2 0)
		4	10.9	10.9	(2 2 0)
		5	8.23	8.20	(1 3 0)
		6	<i>ca.</i> 5.9	_	#1
		1	3.44	—	$(0\ 0\ 1)^n$

<sup>a</sup> #1: Halo of free-rotating phenoxy parts. #2: Halo of free-rotating triphenylmethyl parts. h: stacking distance.  $\rho$ : assumed density (g cm<sup>-3</sup>).

decomposition temperature at *ca.* 500 °C. The derivative **1d** also gave neither I.L. nor the natural texture, and neither did **1a–c**. When **1d** was pressed on the cover slip at r.t., it showed softness with birefringence and spread like boiled Japonica rice. On further heating, it became much softer to form a thinner film by pressing (Fig. 2e). Therefore, **1d** also showed mesomorphism from r.t. Temperature-dependent small angle X-ray diffraction patterns of **1d** at 375 °C gave both sharp and broad peaks (Fig. 3e). The sharp peaks 1–5 in Fig. 3e could be assigned as the reflections of a pseudohexagonal lattice (a = 44.4 Å, b = 25.0 Å,  $a = \sqrt{3}b$ ) from the precise calculation using a reciprocal lattice method.<sup>19</sup> Peak #1 (no. 6) may correspond to the average distance among the freely rotating phenoxy parts. Peak 7 in the high angle region could be assigned to a stacking distance (h = 3.44 Å).

To date, two kinds of pseudohexagonal columnar mesophases,  $Col_{hr}$  (hexagonal–rectangular columnar mesophase) and  $Col_{rh}$  (rectangular–hexagonal columnar mesophase), have been reported. The  $Col_{hr}$  mesophase was firstly reported by Guillon *et al.*<sup>20</sup> In this mesophase, the whole molecules are packed in a 2D hexagonal lattice, whereas the central core parts are packed in a rectangular lattice. On the other hand, the  $Col_{rh}$  mesophase was reported by our group.<sup>21</sup> In this mesophase, the whole molecules are packed in a rectangular lattice, whereas the central core parts are packed in a packed in a 2D hexagonal lattice. These two pseudohexagonal mesophases show different stacking distances.

Since the core part in a  $\text{Col}_{hr}$  mesophase has a rectangular lattice, it shows a long slipped stacking distance of *ca.* 4.0–5.0 Å, like conventional rectangular columnar (Col<sub>r</sub>) mesophases. On the other hand, the core part in a Col<sub>rh</sub> mesophase has a 2D hexagonal lattice; it shows a short face-to-face stacking distance of *ca.* 3.3–3.6 Å, like conventional hexagonal columnar (Col<sub>h</sub>) mesophases. As can be seen from Table 4, the present pseudohexagonal columnar mesophase of **1d** shows a short stacking distance, 3.44 Å, so it could be identified as a Col<sub>rh</sub> mesophase.

Thus, it was revealed that  $(0Ph-PhO)_4PcCu$  (1d) shows a single  $Col_{rh}$  mesophase in a very wide temperature region from r.t. to the decomposition temperature at *ca*. 500 °C. Such a single mesophase of 1d has a great merit for application to organic thin film solar cells, because no phase transition may lead to a stable functionality in solar cells. Hence, the  $(0Ph-PhO)_4PcCu$  (1d) derivative may be the best candidate for application to solar cells.

 $(3Ph-PhO)_8PcCu$  (4). As can be seen from Table 3,  $(3Ph-PhO)_8PcCu$  (4) showed a single crystalline phase (K) from r.t. to the decomposition temperature at *ca*. 470 °C, without melting. Whenever the derivative 4 was pressed on the cover slip until the instrumental limit temperature of 375 °C, it was always rigid (Fig. 2f). The temperature-dependent X-ray diffraction pattern of 4 at 375 °C gave only sharp peaks (Fig. 3f) which are a characteristic of the crystalline phase.



**Fig. 4** Proposed principle of the exhibition of the mesomorphism of the Pc derivative **1a**.

Hereupon, we consider the reason why the  $(3Ph-PhO)_8PcCu$ (4) derivative only shows no mesomorphism. As illustrated in Fig. 4, the tetra-substituted Pc derivatives **1a–d** have free spaces among the neighbouring substituents, so that the substituents may freely rotate to form soft parts necessary to show mesomorphism. On the other hand, the octa-substituted Pc derivative **4** has no free spaces among the neighbouring substituents, so that the substituents may not freely rotate and are prevented from forming soft parts which are essential for mesomorphism.

Thus, the mesomorphism of the present Pc derivatives **1a-d** can originate from free rotation of the bulky substituents.

# Conclusion

We prepared a series of novel bulky group-substituted phthalocyanine (Pc) derivatives, **1a-d** and **4**, and found that the Pc derivatives **1a-d**, but not **4**, show columnar mesomorphism from r.t. to the extremely high decomposition temperatures at 450–500 °C. Their mesomorphism can originate from the thermal fluctuation due to the free rotation of the bulky substituents. Thus, we have systematically demonstrated for the first time that liquid crystals can be also obtained by a series of novel bulky substituents instead of conventional long alkyl chains. Hence, we will be able to obtain a wide variety of new liquid crystalline compounds by using these bulky substituents instead of conventional long alkyl chains. Very interestingly, these are unprecedented guidelines to obtain liquid crystalline compounds.

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