

# Flying-seed-like mesogens 6<sup>†</sup>: Synthesis and mesomorphism of phthalocyanine derivatives substituted by pentafluorosulfanylphenoxy group

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**ABSTRACT:** We have synthesized two novel phthalocyanines, (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**), in order to investigate their flying-seed-like mesomorphism. Their phase transition behaviour and the mesophase structure have been established by using a polarizing optical microscope, a differential scanning calorimeter, and a temperature-dependent small angle X-ray diffractometer. Very interestingly, the derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) substituted a SF<sub>5</sub> group at *m*-position showed a Col<sub>h0</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase from rt to 315.0 °C, whereas the derivative (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**) substituted a SF<sub>5</sub> group at *p*-position showed a crystalline (K) phase from rt to the decomposition temperature at *ca.* 336 °C without showing mesomorphism. Thus, the novel phthalocyanine derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) substituted a strong electron withdrawing SF<sub>5</sub> group at *m*-position shows only one columnar mesophase in a very wide temperature region from rt to 315.0 °C. Furthermore, the Q band wavelengths (672.2 and 672.1 nm) of the present (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**) are shorter than that (680.3 nm) of the previous [(*m*-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5c**) derivative. It can be attributed to strong electron withdrawing nature of the SF<sub>5</sub> group on the phenoxy group.

**KEYWORDS:** flying-seed-like liquid crystals, metallomesogen, phthalocyanine, columnar mesophase.

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## INTRODUCTION

Since the first liquid crystal was found by Reinitzer in 1888 [1], over 100,000 of liquid crystals have been synthesized to date [2]. Almost all the liquid crystalline materials are categorized from the molecular shapes into “calamitic liquid crystals” of rod-like molecules and “discotic liquid crystals” of disk-like molecules [3]. However, each type of the liquid crystals generally consists of a rod-like or disk-like rigid central core and several flexible long alkyl chains in the periphery. When these liquid crystals are heated, the peripheral long alkyl chains first melt to form soft parts and the central cores do not melt to maintain the rigid parts with aggregation each other, it results in showing mesomorphism. Thus, mesomorphism has both characters of the orientation in crystal and the flexibility in liquid. Therefore, it has been long believed that a liquid crystalline molecule needs a rigid central core and flexible long chains in the periphery. However, a very few liquid crystalline compounds out of this general concept have been reported [4-8]. These liquid crystalline compounds have neither a rigid central core nor a flexible long alkyl chain.

In 1911, Vorländer first reported mesomorphism of sodium diphenylacetate (**Ph<sub>2</sub>CHCOONa**: **1** in Fig. 1[A]) having neither a rigid central core nor a flexible long alkyl chain [4]. This compound is totally out of the general category of liquid crystals mentioned above. It shows a mesophase only at very high temperatures, which may have prevented both further investigations of this type of liquid crystals and the precise identification of their mesophases for about 100 years. To our best knowledge, there have been only few reports on this type of liquid crystals by Demus [5], Sanesi [6,7] and Binnemans [8].

In 2006, we revealed by using modern temperature-dependent X-ray diffraction technique that **Ph<sub>2</sub>CHCOONa** (**1**) shows a hexagonal columnar (Col<sub>h</sub>) mesophase, and that this mesomorphism is originated from the excluded volume caused by free rotation of the bulky diphenylmethyl (**Ph<sub>2</sub>CH-**) groups [9]. The rotating bulky **Ph<sub>2</sub>CH-** groups very resemble flying maple seeds, so that we named this liquid crystal as a “flying-seed-like liquid crystal (= mesogen)” [9]. Since this shape of liquid crystals is very different from those of the conventional rod-like and disk-like liquid crystals, it is a new category of liquid crystals.

In 2009, Usoltseva *et al.* reported that a phthalocyanine derivative (**Ph<sub>3</sub>C-PhO**)<sub>4</sub>PcCu (**2a** in Fig. 1) substituted by a bulky triphenylmethyl (**Ph<sub>3</sub>C-**) group instead of long alkyl chains shows mesomorphism [10-11]. The bulky **Ph<sub>3</sub>C-** group in the Pc derivative (**2a**) very resembles the bulky **Ph<sub>2</sub>CH-** group in the previous flying-seed-like liquid crystal **Ph<sub>2</sub>CHCOONa** (**1**). Hence, we thought that the Pc derivative (**2a**) is also one of the flying-seed-like liquid crystals. Accordingly, we synthesized a series of (**X-PhO**)<sub>4</sub>PcCu derivatives (**X = Ph<sub>3</sub>C-**, **Ph<sub>2</sub>MeC-**, **PhMe<sub>2</sub>C-**, **Me<sub>3</sub>C-**: **2a-d** in Fig. 1[B]), and revealed that, according to our expectation, all the derivatives (**2a-d**) also show columnar mesophases from room temperature to ultrahigh temperatures near 500 °C [12]. Furthermore, we synthesized a novel benzoic acid **Me<sub>3</sub>C-PhO•BA** (**3d** in Fig. 1[C]) substituted a bulky **Me<sub>3</sub>C-PhO** group instead of long chain, and revealed that the rod-like dimer of the compound **3d** also shows a nematic mesophase [13]. Moreover, we synthesized the Tb complexes (**X-PhO•BA**)<sub>3</sub>Tb (**4c, d** in Fig. 1[C]) from the corresponding benzoic acid derivatives **3c, d** to show columnar mesophases [13]. Thus, these compounds **2, 3** and **4** were introduced bulky substituents instead of flexible long alkyl chains in the periphery to show mesomorphism. The mesomorphism is attributable to the bulky substituents, which can form the soft parts by the free rotation. Therefore, these compounds are also categorized as flying-seed-like liquid crystals.

Recently, we synthesized a novel series of phthalocyanine derivatives, [(**x-C<sub>1</sub>**)PhO]<sub>8</sub>PcCu (**5a-d**) and [(**x-C<sub>1</sub>**)PhS]<sub>8</sub>PcCu (**6e, f**), substituted by a methoxy group on the phenoxy (or phenylthio) group shown in Table 1 [14,15]. We found that the derivatives, [(*o*-**C<sub>1</sub>**)PhO]<sub>8</sub>PcCu (**5b**), [(*m*-**C<sub>1</sub>**)PhO]<sub>8</sub>PcCu (**5c**), [(*o*-**C<sub>1</sub>**)PhS]<sub>8</sub>PcCu (**6e**) and [(*m*-**C<sub>1</sub>**)PhS]<sub>8</sub>PcCu (**6f**) show columnar mesomorphism, whereas the derivatives, (**PhO**)<sub>8</sub>PcCu (**5a**) having no methoxy

group and [(*p*-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5d**) having a methoxy group at the *p*-position, do not show mesomorphism [14,15]. The mesomorphism of the derivatives, **5b**, **5c**, **6e** and **6f** can be attributed to the bulky substituent (*x*-C<sub>1</sub>)PhY (*x* = *o*, *m*; Y = O, S) forming big excluded volume by the flip-flop. On the other hand, PhO group having no methoxy group and (*p*-C<sub>1</sub>)PhO group having a methoxy group at the *p*-position give so small excluded volume that the derivatives, **5a** and **5d**, cannot show mesomorphism. Thus, we revealed that the mesomorphism depends on the substitution position of the methoxy group on the phenoxy group. This became a good guideline to synthesize future novel flying-seed-like liquid crystal studies.

In 1962, Sheppard synthesized aromatic compounds substituted by pentafluorosulfanyl (SF<sub>5</sub>) group [16-17], but this field has not been actively studied until now. In recent years, pentafluorosulfanyl (SF<sub>5</sub>) group has again attracted our interests, because the SF<sub>5</sub> group has many excellent properties such as high thermal and chemical stabilities, high lipophilicity, high density and strong electron withdrawing ability [18-23]. Therefore, from these excellent properties many applications are expected in the field of organic electronic materials. We have been also attracted by the SF<sub>5</sub> group from a different viewpoint of flying-seed-like liquid crystals. This group is very bulky to afford a large excluded volume [23]. If a novel series of phthalocyanine derivatives, (*x*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (*x* = *o*, *m*, *p*; in Scheme 1), could be synthesized, they would show mesomorphism like as the previous Pc derivatives, [(*x*-C<sub>1</sub>)PhY]<sub>8</sub>PcCu (*x* = *o*, *m*; Y = O, S; in Table 1).

Therefore, in this work we have synthesized a novel series of flying-seed-like liquid crystals based on phthalocyanine derivatives substituted by eight pentafluorosulfanylphenoxy groups, (*x*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (*x* = *o*, *m*, *p*; in Scheme 1), in order to investigate their mesomorphism.

## EXPERIMENTAL

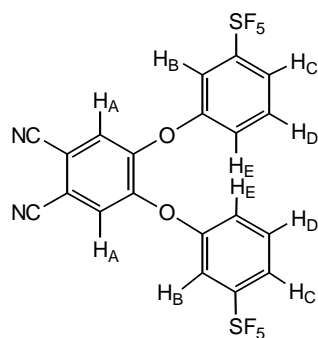
### Synthesis

The present target compounds (*x*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (*x* = *o*, *m*, *p*: **7a-c**) were synthesized according to Scheme 1. The precursor phthalonitrile derivatives, **9a-c**, were prepared by the method of Wöhrle *et al.* [24] using 4,5-dichlorophthalonitrile and *x*-hydroxy(pentafluorosulfanyl)benzene (*x* = 2, 3, 4: **8a-c**) purchased from purchased Tokyo Kasei and Ube Industries, Ltd., respectively. The target Pc derivatives, (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**), could be obtained by cyclic tetramerization reaction of the corresponding phthalonitrile derivatives, **9b** and **9c**, respectively. However, the Pc derivative, (*o*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7a**), substituted by a SF<sub>5</sub> group at *o*-position could not be synthesized from the corresponding phthalonitrile derivative **9a**. It may be attributed to big steric hindrance of the substituent. Therefore, we describe the details of the syntheses only for **9b,c** and **7b,c**. The precursors (**9b**, **c**) were characterized using <sup>1</sup>H-NMR. Elemental analysis data of the Pc derivatives, (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**), were not listed up because these Pc derivatives did not burn out and the observed values were not matched with the calculated ones. It is a common characteristic found in phthalocyanine derivatives. Therefore, the target Pc compounds **7b** and **7c** were identified from the MALDI-TOF mass spectra (Table 2) and the UV-vis spectra (Table 3).

#### *4,5-Bis(3-pentafluorosulfanylphenoxy)phthalonitrile (9b)*

A mixture of 4,5-dichlorophthalonitrile (0.301 g, 1.53 mmol), 3-hydroxy(pentafluorosulfanyl)benzene (**8b**: 0.808 g, 3.67 mmol), dry DMF (8 ml) and potassium carbonate (0.516 g, 3.73 mmol) was heated at 90 °C for 3h with stirring under nitrogen atmosphere. After cooling to rt, the reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in *vacuo*. The residue was purified by column chromatography (silica gel, chloroform, R<sub>f</sub> = 0.58). After removal of the solvent, white powder was obtained (0.628 g, Yield: 73%, mp: 161.3 °C).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ; TMS):  $\delta_{\text{H}}$ , ppm 7.59-7.62 (dd, 2H<sub>C</sub>,  $J_1 = 8.3$  Hz,  $J_2 = 2.0$  Hz, Ar-*H*), 7.48 (t, 2H<sub>D</sub>,  $J = 9.01$  Hz, Ar-*H*), 7.33 (t, 2H<sub>B</sub>,  $J = 2.5$  Hz, Ar-*H*), 7.27 (s, 2H<sub>A</sub>, Ar-*H*), 7.08 (dd, 2H<sub>E</sub>,  $J_1 = 8.1$  Hz,  $J_2 = 2.0$  Hz, Ar-*H*)



#### **4,5-Bis(4-pentafluorosulfonylphenoxy)phthalonitrile (9c)**

A mixture of 4,5-dichlorophthalonitrile (0.302 g, 1.53 mmol), 4-hydroxy(pentafluorosulfonyl)benzene (**8c**: 0.809 g, 3.67 mmol), dry DMF (8 ml) and potassium carbonate (0.515 g, 3.73 mmol) was heated at 90 °C for 3h with stirring under nitrogen atmosphere. After cooling to rt, the reaction mixture was extracted with chloroform and washed with water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated in *vacuo*. The residue was purified by column chromatography (silica gel, chloroform,  $R_f = 0.58$ ). After removal of the solvent, white powder was obtained (0.722 g, Yield: 84%, mp: 135.6 °C).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS):  $\delta_{\text{H}}$ , ppm 7.82~7.86 (m, 4H, Ar-*H*), 7.44 (s, 2H, Ar-*H*), 7.07 (m, 4H, Ar-*H*).

#### **(*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (7b•4HexOH)**

A mixture of 4,5-bis(3-pentafluorosulfonylphenoxy)phthalonitrile (**9b**: 0.302 g, 0.534 mmol), 1-hexanol (9 ml),  $\text{CuCl}_2$  (0.0201 g, 0.149 mmol) and DBU (3 drops) was refluxed under nitrogen atmosphere for 2.5h. After cooling to rt, methanol was poured into the reaction mixture to precipitate the target compound. The solvents were removed by filtration. The residue was washed with methanol, ethanol and chloroform successively. The residue was resolved in a small amount of THF, and it was put into a column (silica gel). It was purified by column chromatography by using chloroform ( $R_f = 0.0$ ) as the first eluent to remove the impurities and then by using THF ( $R_f = 1.0$ ) as the second eluent to collect the target Pc compound. After removal of the solvent, a small amount of THF solution of the residue was dropped into a large amount of chloroform to precipitate it for four times, and then into methanol to precipitate it for two times to afford blue solid of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (0.163 g, Yield: 45%).

MALDI-TOF mass spectral data: See Table 2.

UV-Vis spectra data: See Table 3.

Phase transition temperatures: See Table 4.

#### **(*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (7c)**

A mixture of 4,5-bis(4-pentafluorosulfonylphenoxy)phthalonitrile (**9c**: 0.401 g, 0.710 mmol), 1-hexanol (6 ml),  $\text{CuCl}_2$  (0.0269 g, 0.200 mmol) and DBU (3 drops) was refluxed under nitrogen atmosphere for 3h. After cooling to rt, methanol was poured into the reaction mixture to precipitate the target Pc compound. The solvents were removed by filtration. The residue was washed with methanol, ethanol and chloroform successively. The residue was resolved in a small amount of THF, and it was put into a column (silica gel). It was purified by column chromatography by using chloroform ( $R_f = 0.0$ ) as the first eluent to remove the impurities and then by using THF ( $R_f = 0.95$ ) as the second eluent to collect the target Pc compound. After removal of the solvent, a small amount of THF solution of the residue was dropped into a large amount of methanol to precipitate it for three times to afford blue solid of (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (0.212 g, Yield: 51%).

MALDI-TOF mass spectral data: See Table 2.

UV-Vis spectra data: See Table 3.

Phase transition temperatures: See Table 4.

## Measurements

The  $^1\text{H-NMR}$  measurements were carried out by using  $^1\text{H-NMR}$  (Bruker Ultrashield 400 M Hz). The MALDI-TOF mass spectral measurements were carried out by using a Bruker Daltonics Autoflex III spectrometer (matrix: dithranol). Electronic absorption (UV-vis) spectra were recorded by using a Hitachi U-4100 spectrophotometer. Phase transition behaviour of the present compounds was observed with polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP90 Central Processor, a Rigaku Thermo Plus TG8120 thermal gravity analyser (TGA) and a Shimadzu DSC-50 differential scanning calorimeter. The mesophases were identified by using a small angle X-ray diffractometer (Bruker Mac SAXS System) equipped with a temperature-variable sample holder adopted a Mettler FP82HT hot stage. The measurable range is from 3.0 Å to 110 Å and the temperature range is from rt to 375 °C.

## RESULTS AND DISCUSSION

### Electronic absorption spectra

Fig. 2 shows the UV-vis spectra of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7b**) and  $(p\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7c**) in THF and these spectral data were summarized in Table 3. As can be seen from this Table 3, the Q band of **7b** and **7c** were at 672.2 and 672.1 nm, respectively. These Q bands of the present  $(x\text{-SF}_5\text{PhO})_8\text{PcCu}$  ( $x = m, p$ : **7b, c**) derivatives are shorter than that (680.3 nm) of the previous  $[(m\text{-C}_1)\text{PhO}]_8\text{PcCu}$  (**5c**) derivative. It can be attributed to strong electron withdrawing nature of the  $\text{SF}_5$  group on the phenoxy group. Furthermore, the  $(p\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7c**) derivative gave an additional broad peak at 771.5 nm in the longer wavelength region. This peak may be originated from the axial coordination of Cu(II) ion by the solvent THF molecules [25-26].

### Phase transition behaviour

Table 4 lists up the phase transition temperatures and enthalpy changes of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7b**) and  $(p\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7c**). The phase transition behaviour was established by using thermal gravity analysis (TGA), differential scanning calorimetry (DSC), polarizing optical microscope (POM) and temperature-dependent small angle X-ray diffraction measurements.

#### TGA and DSC measurements

Fig. 3 shows the TGA and DSC thermograms of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (**7b**). The freshly prepared (virgin) sample of **7b** contains four 1-hexanol (HexOH) molecules as the crystal solvent. The number of 1-hexanol molecules could be confirmed from TGA thermogram shown in Fig. 3. As can be seen from the DSC thermogram in this figure, the virgin sample of **7b** gave a very broad endothermic peak at *ca.* 100–200 °C in the first heating run, whereas the broad peak disappeared in the second heating run. This broad endothermic peak in the DSC thermogram corresponds to the large loss of the weight in the TGA thermogram. The weight loss matched to evaporation of just four HexOH molecules. Hence, the virgin sample of **7b** contains four HexOH molecules as the crystal solvent, whereas the non-virgin sample gives pure  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7b**) without the crystal solvent. The crystal solvent was observed only for  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7b**) substituted by a  $\text{SF}_5$  group at the *m*-position, but not for  $(p\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7c**) substituted by a  $\text{SF}_5$  group at the *p*-position.

### Mesomorphism

As can be seen from Table 4, the virgin sample of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (**7b•4HexOH**) showed a crystalline (K<sub>v</sub>) phase at room temperature (rt). When it was heated from rt, the K<sub>v</sub> phase transformed into another crystalline K<sub>2</sub> phase at 48.5 °C and then the K<sub>2</sub> phase melted at 69.0 °C into a rectangular ordered columnar (Col<sub>ro1</sub>(P2<sub>1</sub>/a) (=p2gg)) mesophase with containing the HexOH crystal solvent. On further heating, the crystal solvent evaporated at *ca.* 100~200 °C and the resulted pure derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) showed another rectangular ordered columnar Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase. When it was heated up to 315.0 °C, the Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase cleared into isotropic liquid (I.L.) with accompanying gradual decomposition (dc.). When the Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase below the clearing point was directly cooled down to rt, it remained as the Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase without any phase transitions. Thus, the derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) substituted a SF<sub>5</sub> group at *m*-position showed mesomorphism. On the other hand, the derivative (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**) substituted a SF<sub>5</sub> group at *p*-position showed a crystalline (K) phase from rt to the decomposition temperature at *ca.* 336 °C without showing mesomorphism.

Very interestingly, it corresponds to the previous result that the [(*m*-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5c**) derivative substituted a methoxy group at *m*-position shows mesomorphism but the [(*p*-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5d**) derivative substituted a methoxy group at *p*-position does not, as shown in Table 1 [14].

### Polarizing optical microscopic observations

Fig. 4 shows photomicrographs of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (**7b•4HexOH**) at rt and 80 °C, and (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) at 310 °C. As can be seen from Fig. 4[A], the virgin sample was crystalline (K<sub>v</sub>) phase at rt. When it was heated at 80 °C and the cover glass plate was pressed, it was spread out to show stickiness together with birefringence, as can be seen from Fig. 4[B]. Thus, the mesomorphism of the virgin sample at 80 °C was confirmed. When the I.L. over 315 °C was quickly cooled down to 310 °C with avoiding the decomposition, a texture of the Col<sub>ro2</sub>(P2/a) mesophase could be observed, as shown in Fig. 4[C].

### Temperature-dependent X-ray diffraction measurements

Fig. 5[A] shows the X-ray diffraction pattern of the virgin sample of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (**7b•4HexOH**) at 80 °C. As can be seen from this pattern, **7b•4HexOH** gave fourteen reflection peaks. By using Reciprocal Lattice Calculation Method [27], all the peaks except for Peak no. 9 could be well assigned to the reflections from a 2D rectangular lattice with a P2<sub>1</sub>/a (=p2gg) symmetry having the lattice constants of *a* = 38.4 Å and *b* = 26.2 Å. Peak no. 9 could be assigned to the stacking distance, *h* = 4.82 Å. Therefore, this mesophase could be identified as Col<sub>ro1</sub>(P2<sub>1</sub>/a) (=p2gg). On the other hand, when it was heated to 220 °C and then cooled into rt, it gave the non-virgin sample of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) having no crystal solvents. Fig. 5[B] shows the X-ray diffraction pattern of the non-virgin sample at rt. This pattern gave eighteen reflection peaks. All the peaks except for Peak no. 12 could be well assigned to the reflections from a 2D rectangular lattice with a P2<sub>1</sub>/a (=p2gg) symmetry having the lattice constants of *a* = 36.6 Å and *b* = 26.5 Å. Peak no. 12 could be assigned to the stacking distance, *h* = 4.88 Å. Therefore, this mesophase could be identified as another (Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase.

All the X-ray data were summarized in Table 5. As can be seen from this table, the *b* lattice constants are almost the same but the *a* lattice constants are different in these two Col<sub>ro</sub>(P2<sub>1</sub>/a) (=p2gg) mesophases of **7b•4HexOH** and **7b**. The lattice constant *a* for the Col<sub>ro1</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase of **7b•4HexOH** expands by 1.8 Å in comparison with that of **7b**. It is attributable to the inclusion of four HexOH molecules as the crystal solvent in the virgin sample of **7b•4HexOH**.

As can be seen also from Table 5, the mesophases, Col<sub>ro1</sub>(P2<sub>1</sub>/a) (=p2gg) and Col<sub>ro2</sub>(P2<sub>1</sub>/a) (=p2gg), gave very high densities of  $\rho = 1.9$  and  $1.6 \text{ g/cm}^3$ , respectively. Although these densities are very high in comparison with the densities

usually observed at about 1.0 g/cm<sup>3</sup> for general columnar mesophases, these densities can be proven as a proper value from Z Value Calculation [27].

The number (Z) of molecules in a lattice can be calculated from the stacking distance ( $h = 4.88 \text{ \AA}$ ) and the lattice constants of 2D rectangular lattice ( $a = 36.6 \text{ \AA}$  and  $b = 26.5 \text{ \AA}$ ) for **7b** listed in Table 5. When  $\rho$ , V, N and M are density of mesophase, volume of unite lattice, Avogadro's number and molecular weight, respectively, Z value can be obtained from following equation:

$$Z = (\rho VN)/M = [\rho(a \times b \times h)N]/M$$

The theoretical number of molecules in a 2D rectangular lattice having P2<sub>1</sub>/a (=p2gg) symmetry is Z = 2.0. Therefore, the density can be calculated from following equation:

$$\begin{aligned}\rho &= ZM/[a \times b \times h]N \\ &= 2.0 \times 2321.21(\text{g/mol}) / [(36.6 \times 10^{-8} \text{ cm}) \times (26.5 \times 10^{-8} \text{ cm}) \times (4.88 \times 10^{-8} \text{ cm})] \times 6.02 \times 10^{23}(\text{mol}) \\ &= 1.63(\text{g/cm}^3) \\ &\approx 1.6(\text{g/cm}^3)\end{aligned}$$

Therefore, this high density  $\rho = 1.6 \text{ (g/cm}^3\text{)}$  is a rationally proper value.

The difference between 1.6 and 1.9 g/cm<sup>3</sup> may be resulted from the crystal solvent. As can be seen from Table 5, the lattice constants of the Col<sub>ro</sub> mesophase of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (**7b•4HexOH**) are not so different from those of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**). Four HexOH molecules are compacted in a similar size of lattice, so that the density of the Col<sub>ro</sub> mesophase of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu•4HexOH (**7b•4HexOH**) may be much higher than that of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**). These high densities of the mesophases may be originated from the high density of eight SF<sub>5</sub> groups in a molecule.

## CONCLUSION

In this study, we have synthesized two novel phthalocyanines, (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**), in order to investigate their flying-seed-like mesomorphism. Very interestingly, the desolvated derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) substituted a SF<sub>5</sub> group at *m*-position showed a Col<sub>ro</sub>(P2<sub>1</sub>/a) (=p2gg) mesophase from rt to 315.0 °C, whereas the derivative (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**) substituted a SF<sub>5</sub> group at *p*-position showed a crystalline (K) phase from rt to the decomposition temperature at *ca.* 336 °C without showing mesomorphism. The mesophase shows a very high density  $\rho = 1.6 \text{ g/cm}^3$  in comparison with the densities usually observed at about 1.0 g/cm<sup>3</sup> for general columnar mesophases. It may be originated from the high density of eight SF<sub>5</sub> groups in a molecule. Furthermore, the Q band wavelengths (672.2 and 672.1 nm) of the present (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**) are shorter than that (680.3 nm) of the previous [(*m*-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5c**) derivative. It can be attributed to strong electron withdrawing nature of the SF<sub>5</sub> group on the phenoxy group.

Thus, the novel phthalocyanine derivative (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) substituted a strong electron withdrawing SF<sub>5</sub> group at *m*-position shows only one columnar mesophase in a very wide temperature region from rt to 315.0 °C. It is very favourable for the applications as organic electronic materials, because the electrical properties may be stable and constant due to no phase transitions.

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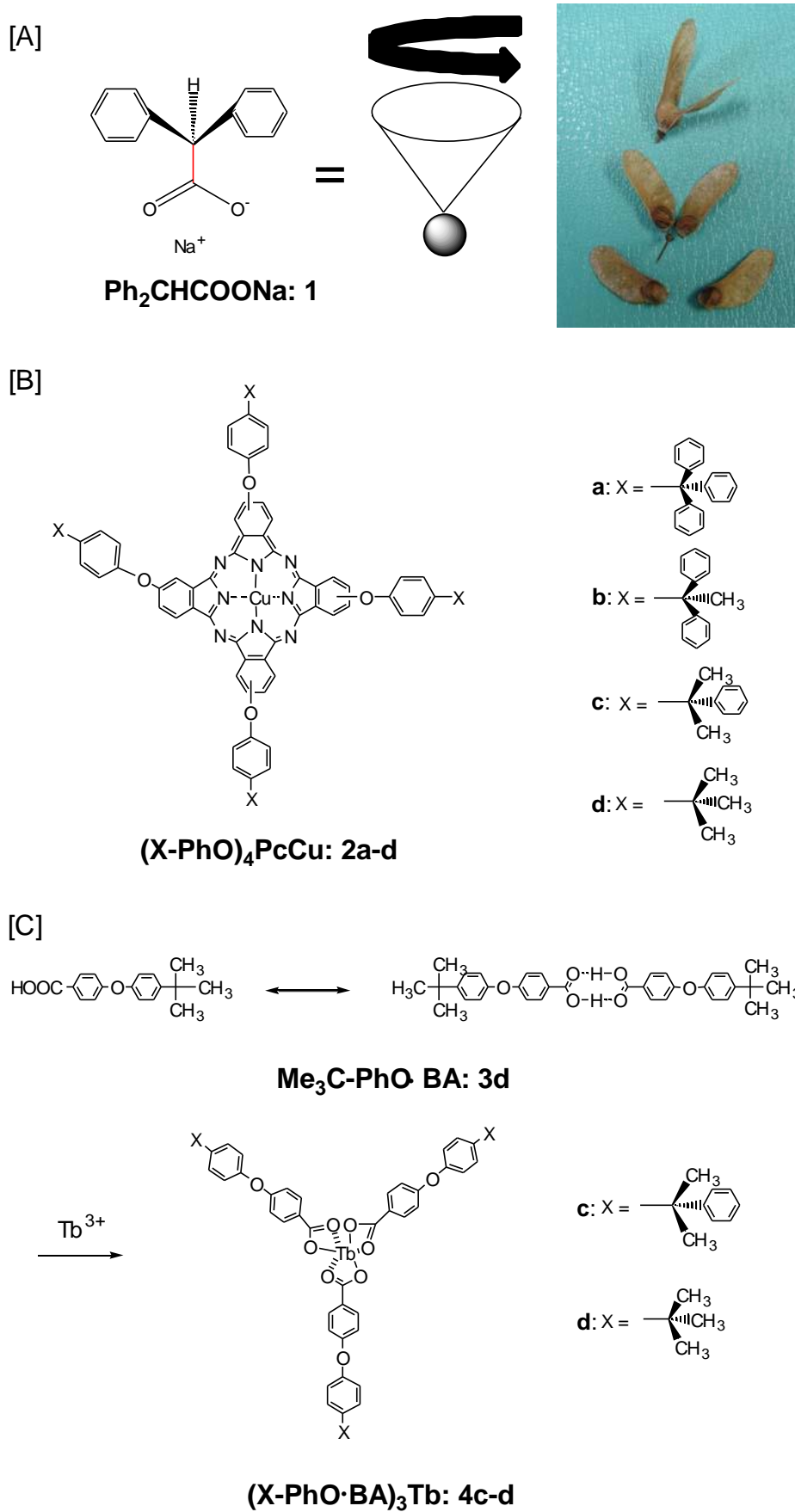
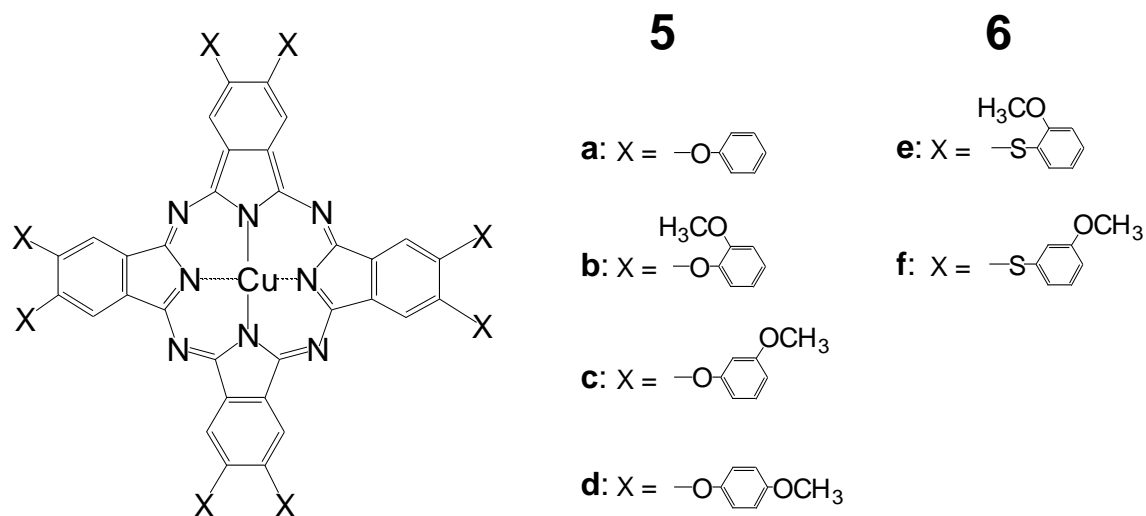


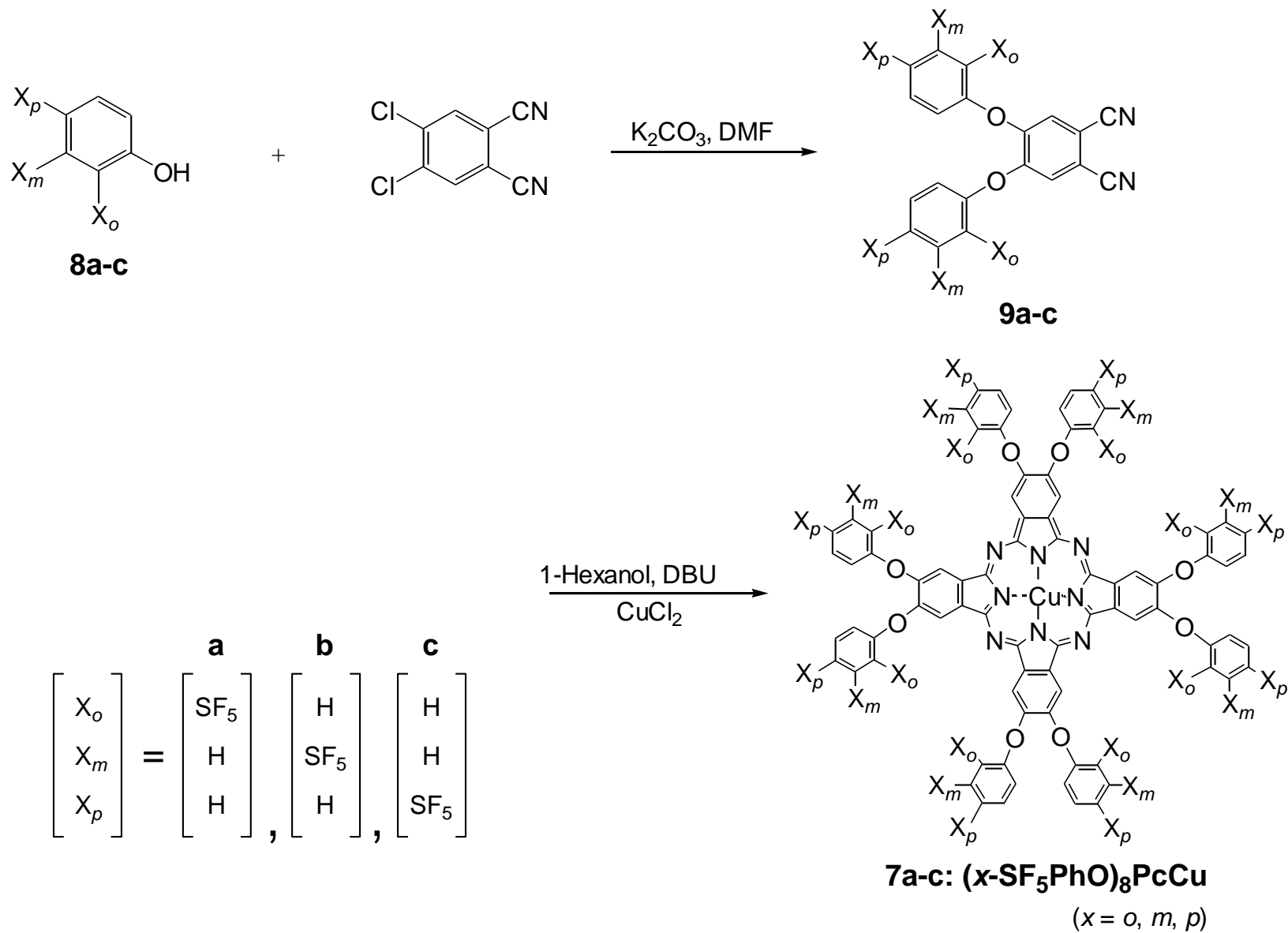
Fig. 1. Flying-seed-like liquid crystal compounds synthesized to date.

Table 1. Phase transition sequences of the previously reported flying-seed-like phthalocyanine derivatives, [(X-C<sub>1</sub>)PhO]<sub>8</sub>PcCu (**5a-d**) and [(X-C<sub>1</sub>)PhS]<sub>8</sub>PcCu (**6e-f**).



Compounds	Phase	$T$ (°C) [ $\Delta H$ (kJmol <sup>-1</sup> )]	Phase	relaxation
<b>5a: (PhO)<sub>8</sub>PcCu</b> 			K	541 → dc.
<b>5b: [(o-C<sub>1</sub>)PhO]<sub>8</sub>PcCu</b> 	Glassy Col <sub>ro</sub> (P2m)	T <sub>g</sub> = 87.4 177.3 [7.20] 299.4 [19.0]	K <sub>1</sub> → K <sub>2</sub>	402 → I.L. (1st dc.) → 2nd dc.
<b>5c: [(m-C<sub>1</sub>)PhO]<sub>8</sub>PcCu</b> 	Glassy Col <sub>ro</sub> (P2 <sub>1/a</sub> )	T <sub>g</sub> = 69.9 191.3 [13.4] 255.1 [2.69] 360.1 [10.7]	K <sub>1</sub> → Col <sub>ro1</sub> (P2 <sub>1/a</sub> ) → Col <sub>ro2</sub> (P2 <sub>1/a</sub> )	405 → M <sub>x</sub> (1st dc.) → 2nd dc.
<b>5d: [(p-C<sub>1</sub>)PhO]<sub>8</sub>PcCu</b> 			K	363 → dc.
<b>6e: [(o-C<sub>1</sub>)PhS]<sub>8</sub>PcCu</b> 	K <sub>1</sub>	T <sub>g</sub> = 180 301.7 [50.1] 314.9 [7.77]	K <sub>2</sub> → K <sub>3</sub>	362.9 [2.90] → Col <sub>tet.o</sub> → I.L. (dc.)
<b>6f: [(m-C<sub>1</sub>)PhS]<sub>8</sub>PcCu</b> 	K <sub>1</sub>	T <sub>g</sub> = 180 287.4 [3.78]	K <sub>2</sub>	334.2 [6.72] → Col <sub>ro</sub> (P2m) → I.L. (dc.)

Phase nomenclature: K = crystal, Col<sub>ro</sub> = rectangular ordered columnar mesophase, M<sub>x</sub> = unidentified mesophase, Col<sub>tet.o</sub> = tetragonal ordered columnar, I.L. = isotropic liquid and dc. = decomposition. The symmetries of P2m and P2<sub>1/a</sub> corresponds to p2mg and p2gg, respectively.



Scheme 1. Synthetic route for  $(x\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7a-c**). DMA = N,N'-dimethylacetamide and DBU = 1,8-diazabicyclo[5,4,0]-undec-7-ene.

Table 2. MALDI-TOF mass spectral data and yields of (*o*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7a**), (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**).

Compound	Mol. formula (Mol. wt)	Exact mass formula (m/z = M+1)	Exact mass observed (m/z = M+1)	Yield (%)
<b>7a: (<i>o</i>-SF<sub>5</sub>PhO)<sub>8</sub>PcCu</b>	C <sub>80</sub> H <sub>40</sub> F <sub>40</sub> N <sub>8</sub> O <sub>8</sub> S <sub>8</sub> Cu (2321.21)	—	—	Not obtained
<b>7b: (<i>m</i>-SF<sub>5</sub>PhO)<sub>8</sub>PcCu</b>	C <sub>80</sub> H <sub>40</sub> F <sub>40</sub> N <sub>8</sub> O <sub>8</sub> S <sub>8</sub> Cu (2321.21)	2318.94	2318.77	44.7
<b>7c: (<i>p</i>-SF<sub>5</sub>PhO)<sub>8</sub>PcCu</b>	C <sub>80</sub> H <sub>40</sub> F <sub>40</sub> N <sub>8</sub> O <sub>8</sub> S <sub>8</sub> Cu (2321.21)	2318.94	2319.04	51.4

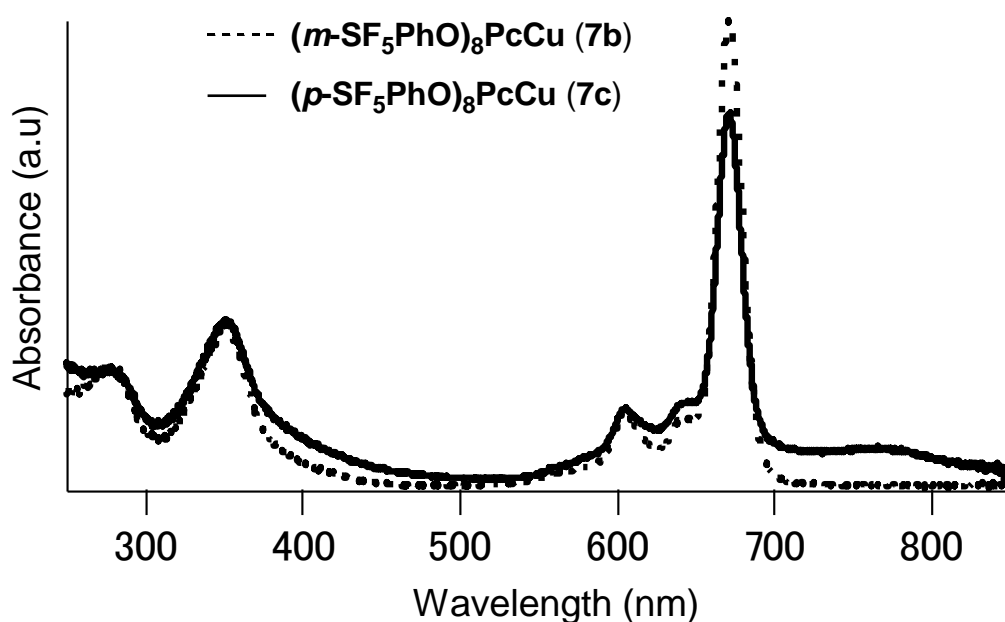


Fig. 2. UV-vis spectra in THF at room temperature of compounds **7b** and **7c**.

Table 3. UV-vis spectral data of (*m*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7b**) and (*p*-SF<sub>5</sub>PhO)<sub>8</sub>PcCu (**7c**).

Compound	Concentration <sup>#</sup> (X10 <sup>-5</sup> mol/l)	$\lambda_{\max}$ (nm) (log $\epsilon$ )					
		Soret-band		Q <sub>0-1</sub> band	*	Q <sub>0-0</sub> band	
<b>5c: [(<i>m</i>-C<sub>1</sub>)PhO]<sub>8</sub>PcCu</b>	0.50	281.3 (4.82)	355.8 (4.90)	613.2 (4.62)	653.0 (4.60) <sup>0</sup>	680.3 (5.41)	-
<b>7b: (<i>m</i>-SF<sub>5</sub>PhO)<sub>8</sub>PcCu</b>	0.51	279.9 (4.87)	351.9 (5.01)	605.9 (4.68)	644.2 (4.64) <sup>0</sup>	672.2 (5.47)	-
<b>7c: (<i>p</i>-SF<sub>5</sub>PhO)<sub>8</sub>PcCu</b>	0.50	277.4 (4.88)	349.9 (5.03)	605.9 (4.70)	642.6 (4.73) <sup>0</sup>	672.1 (5.38)	771.5 (4.40) <sup>**</sup>

#: In THF. \*: Aggregation band of Q<sub>0-0</sub> band. \*\*: Axial coordination to Cu(II) ion by the solvent molecules. <sup>0</sup>: Shoulder.

Table 4. Phase transition temperatures and enthalpy changes of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (**7b** $\cdot 4\text{HexOH}$ ) and  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7c**).

Compound	Phase	$T/^\circ\text{C}$ [ $\Delta H(\text{kJmol}^{-1})$ ]	Phase
<b>7b: <math>(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}</math></b>	$\text{K}_{1v}$	$48.5$ [ $13.1$ ]	$\text{K}_2$
	$\text{K}_2$	$69.0$ [ $3.36$ ]	$\text{Col}_{ro1}$ ( $\text{P2}_1/\text{a}$ ) (=p2gg)
	$\text{Col}_{ro1}$ ( $\text{P2}_1/\text{a}$ ) (=p2gg)	ca. 100–200 -4HexOH	$\text{Col}_{ro2}$ ( $\text{P2}_1/\text{a}$ ) (=p2gg)
		$315.0$ [ $43.6$ ]	I.L. (gradually dc.)
<b>7c: <math>(p\text{-SF}_5\text{PhO})_8\text{PcCu}</math></b>			
	K	ca. 336	dc.

Phase nomenclature: K = crystal,  $\text{Col}_{ro}$  = recutangular ordered columnar mesophase, I.L. = isotropic liquid, dc. = decomposition and v = virgin sample.

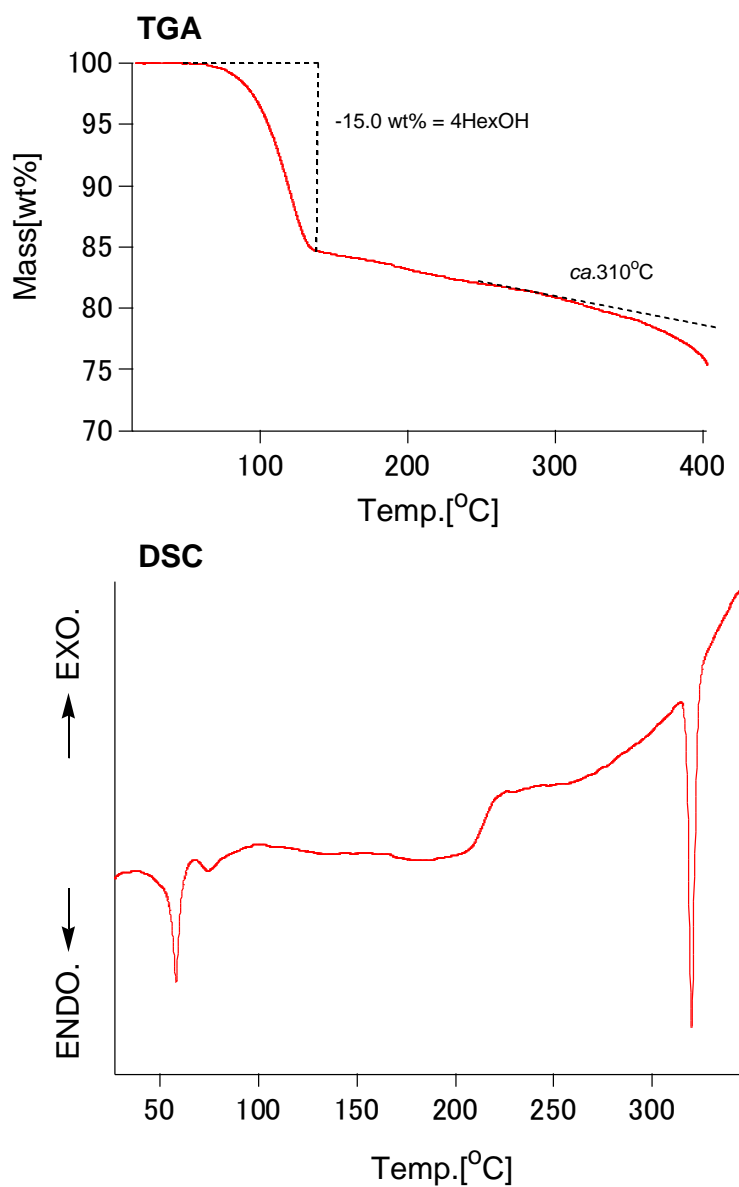
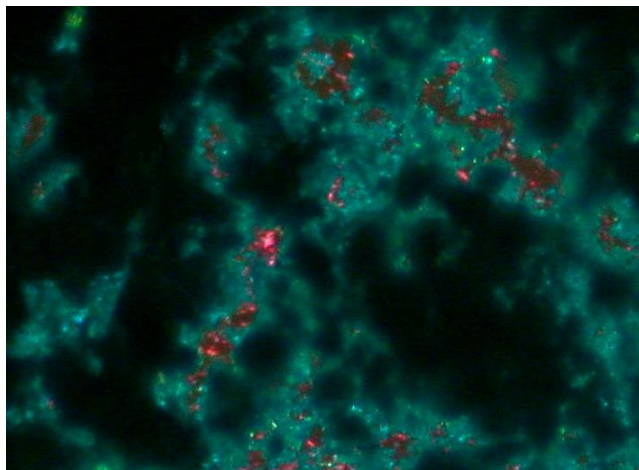


Fig. 3. TGA and DSC thermograms of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (**7b** $\cdot 4\text{HexOH}$ ).

[A] K at rt



[B]  $\text{Col}_{\text{ro1}}(\text{P2}_1/\text{a})$  ( $=\text{p2gg}$ ) at 80 °C



[C]  $\text{Col}_{\text{ro2}}(\text{P2}_1/\text{a})$  ( $=\text{p2gg}$ ) at 310 °C

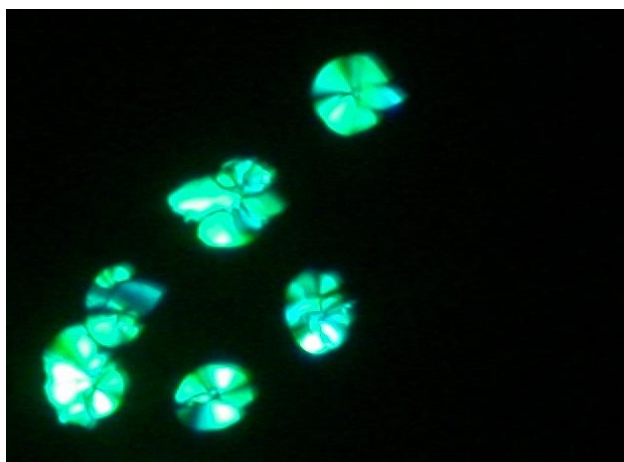
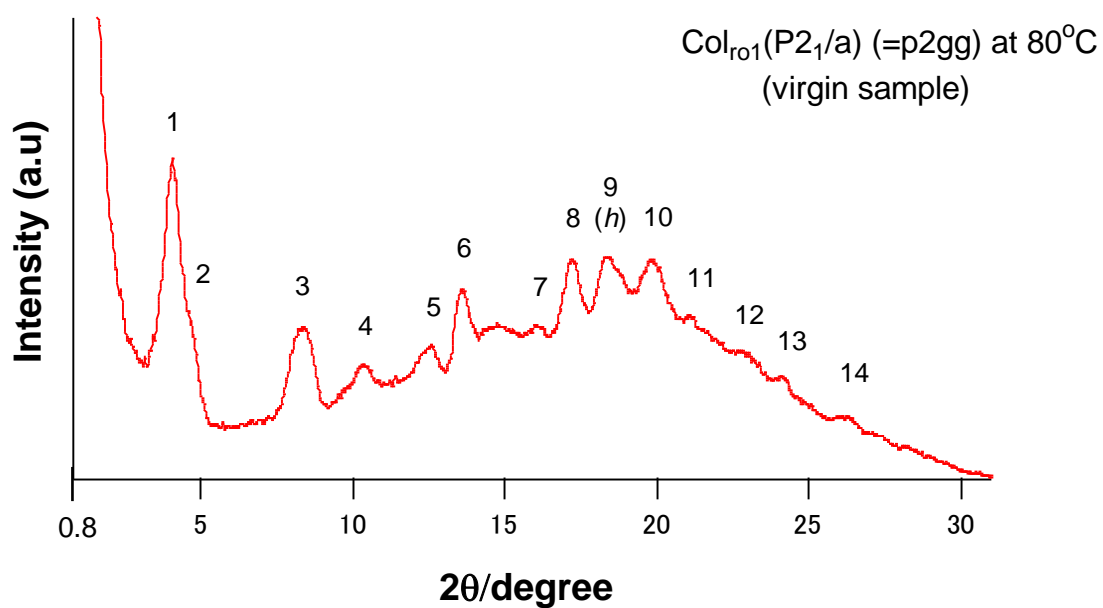


Fig. 4. Photomicrographs of [A] the crystalline phase K and [B] the  $\text{Col}_{\text{ro1}}(\text{P2}_1/\text{a})$  ( $=\text{p2gg}$ ) mesophase of (*m*- $\text{SF}_5\text{PhO}$ ) $_8\text{PcCu}\cdot 4\text{HexOH}$  (**7b** $\cdot 4\text{HexOH}$ ), and [C] the  $\text{Col}_{\text{ro2}}(\text{P2}_1/\text{a})$  ( $=\text{p2gg}$ ) mesophase of (*m*- $\text{SF}_5\text{PhO}$ ) $_8\text{PcCu}$  (**7b**).

[A]  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (7b $\cdot$ 4HexOH)



[B]  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (7b)

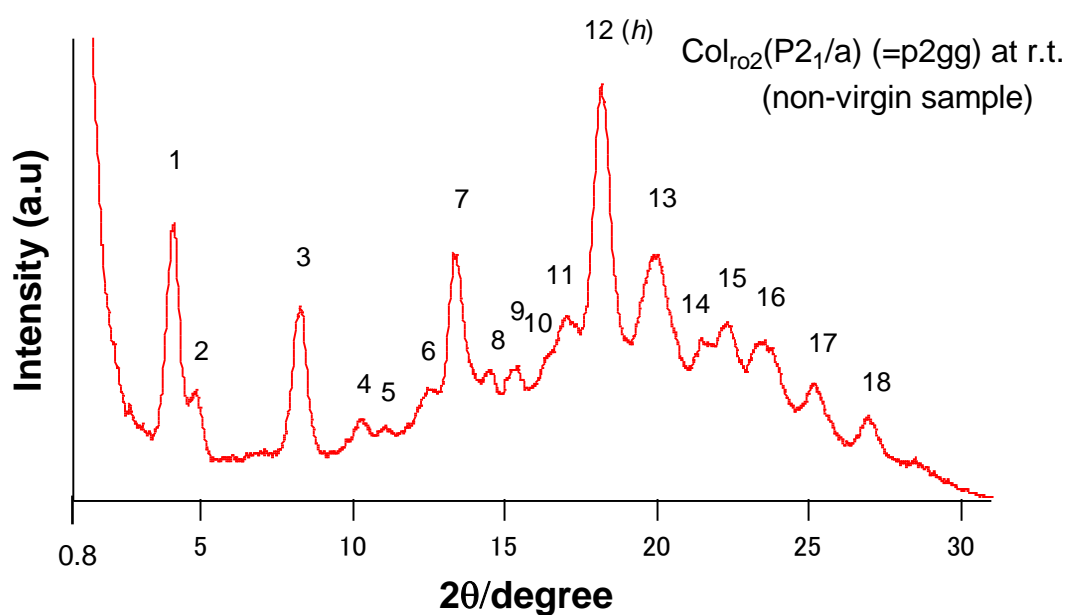


Fig. 5. Small angle X-ray diffraction patterns of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (7b $\cdot$ 4HexOH) and  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (7b).

Table 5. X-Ray data of  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}$  (**7b** $\cdot 4\text{HexOH}$ ) and  $(m\text{-SF}_5\text{PhO})_8\text{PcCu}$  (**7b**).

Compound (mesophase) Lattice constants/Å	Peak No.	Spacing/Å		Miller indices ( <i>h k l</i> )
		Observed	Calculated	
<b><math>(m\text{-SF}_5\text{PhO})_8\text{PcCu}\cdot 4\text{HexOH}</math> (<b>7b</b><math>\cdot 4\text{HexOH}</math>)</b>				
(Col <sub>ro1</sub> (P2 <sub>1</sub> /a) (= p2gg) at 80°C) of virgin sample  a = 38.4. b = 26.2 h = 4.82 Z = 2.0 for $\rho = 1.9$	1	21.6	21.6	(1 1 0)
	2	19.2	19.2	(2 0 0)
	3	10.7	10.8	(2 2 0)
	4	8.51	8.51	(1 3 0)
	5	7.17	7.22	(3 3 0)
	6	6.49	6.46	(4 3 0)
	7	5.50	5.41	(4 4 0)
	8	5.16	5.16	(6 3 0)
	9	4.82	4.82	(0 0 1) <sup>h</sup>
	10	4.48	4.51	(8 2 0)
	11	4.19	4.21	(7 4 0)
	12	3.88	3.87	(8 4 0)
	13	3.69	3.67	(2 7 0)
	14	3.40	3.42	(7 6 0)
<b><math>(m\text{-SF}_5\text{Ph})_8\text{PcCu}</math> (<b>7b</b>)</b>				
(Col <sub>ro2</sub> (P2 <sub>1</sub> /a) (= p2gg) at r.t.) of non-virgin sample  a = 36.6. b = 26.5 h = 4.88 Z = 2.0 for $\rho = 1.6$	1	21.5	21.5	(1 1 0)
	2	18.3	18.3	(2 0 0)
	3	10.7	10.7	(2 2 0)
	4	8.58	8.58	(1 3 0)
	5	8.01	8.01	(2 3 0)
	6	7.10	7.06	(5 1 0)
	7	6.62	6.62	(0 4 0)
	8	6.10	6.10	(6 0 0)
	9	5.77	5.82	(3 4 0)
	10	5.42	5.37	(4 4 0)
	11	5.20	5.24	(1 5 0)
	12	4.88	4.88	(0 0 1) <sup>h</sup>
	13	4.45	4.42	(0 6 0)
	14	4.14	4.15	(3 6 0)
	15	3.98	3.98	(4 6 0)
	16	3.78	3.78	(5 6 0)
	17	3.53	3.50	(4 7 0)
	18	3.31	3.31	(0 8 0)

*h* = Stacking distance between the monomers.  $\rho$ : assumed density (g/cm<sup>3</sup>).