

Flying-seed-like Liquid Crystals 7[†]: Synthesis and Mesomorphism of Novel Octakis(*m*-chloropyridyloxy)phthalocyanato copper(II) Complexes

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ABSTRACT: We have synthesized three novel octakis(*m*-chloropyridyloxy)phthalocyaninato copper(II) complexes, $[\text{x-PyO}(\textit{m}\text{-Cl})]_8\text{PcCu}$ ($x = 2, 3, 4$: **2a-c**), keeping a chlorine atom at the *meta* position on the 2-, 3- and 4-pyridyloxy group, in which the nitrogen atom is located at the 2-, 3- and 4-positions, respectively. 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 mesomorphism appears with strong dependence of the position of nitrogen in *m*-chloropyridyloxy group. The derivative $[\text{3-PyO}(\textit{m}\text{-Cl})]_8\text{PcCu}$ (**2b**) introduced a nitrogen atom at the 3-position is not mesogenic but crystalline. On the other hand, the derivative $[\text{2-PyO}(\textit{m}\text{-Cl})]_8\text{PcCu}$ (**2a**) introduced a nitrogen atom at the 2-position shows columnar mesomorphism only at very high temperatures over 325 °C. The derivative $[\text{4-PyO}(\textit{m}\text{-Cl})]_8\text{PcCu}$ (**2c**) introduced a nitrogen atom at the 4-position shows columnar mesomorphism in a very wide temperature region from rt to the decomposition temperature at 306 °C. From the viewpoint of N...Cl halogen bond, we have discussed about relationship between their mesomorphism and the position of nitrogen atom in *m*-chloropyridyloxy group.

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

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INTRODUCTION

In our laboratory, we have developed a new type of “flying-seed-like liquid crystals” since 2006.¹⁻⁶ Very recently, we have synthesized novel phthalocyanine derivatives, $[(x-C_1)PhO]_8PcCu$ ($x = p, o, m$: **1a-c** in Figure 1), substituted by eight phenoxy groups having methoxy groups on their *para*, *ortho*, or *meta* positions.⁴ As a result, $[(p-C_1)PhO]_8PcCu$ (**1a**) shows no mesophase, whereas $[(o-C_1)PhO]_8PcCu$ (**1b**) shows a monotropic $Col_{r0}(P2m)$ mesophase; $[(m-C_1)PhO]_8PcCu$ (**1c**) shows two enantiotropic $Col_{r0}(P2_1/a)$ columnar mesophases in a wide temperature region. Thus, we have revealed that mesomorphism could be induced by these novel bulky substituents instead of using long alkyl chains, and that appearance of the mesomorphism was greatly affected by the position of methoxy groups. Especially, it is very interesting that the derivative **1c** having a methoxy group at the *meta* position tends to show enantiotropic mesophases, whereas the derivative **1a** having a methoxy group at the *para* position tends to show no mesophase.

Therefore, in this study, we have synthesized novel octakis-(*m*-chloropyridyloxy)phthalocyaninato copper(II) complexes, $[x-PyO(m-Cl)]_8PcCu$ ($x = 2, 3, 4$: **2a-c** in Scheme 1), keeping a chlorine atom at the *meta* position on the 2-, 3- and 4-pyridyloxy group, in which the nitrogen atom is located at the 2-, 3- and 4-positions, respectively, and investigated the influence of the position of nitrogen atom in the *m*-chloropyridyloxy group on their mesomorphism.

EXPERIMENTAL

Synthesis

Scheme 1 shows synthetic route for novel flying-seed-like liquid crystals based on $[x-PyO(m-Cl)]_8PcCu$ (**2a-c**: $x=2, 3, 4$). They were prepared according to our previously reported methods.¹² Phthalonitrile derivatives, $[x-PyO(m-Cl)]_2FN$ (**3a-c**: $x=2, 3, 4$), were synthesized from 4,5-dichlorophthalonitrile and the corresponding *m*-halogenohydroxy pyridine derivatives, $x-PyOH(m-Cl)$ ($x=2, 3, 4$), purchased from Tokyo Kasei. The target phthalocyanine derivatives, $[x-PyO(m-Cl)]_8PcCu$ (**2a-c**: $x=2, 3, 4$), could be synthesized from the corresponding phthalonitrile derivatives, $[x-PyO(m-Cl)]_2FN$ (**3a-c**: $x=2, 3, 4$). The detailed synthetic procedures were described below.

$[2-PyO(m-Cl)]_2FN$ (**3a**)

A mixture of 4, 5-dichlorophthalonitrile(104 mg, 0.525 mmol), 6-chloro-2-pyridine (175 mg, 1.35 mmol) and dry-DMSO (5 ml) was stirred at 60 °C under a nitrogen atmosphere for 10 min. To the reaction mixture, one sixth of K_2CO_3 (484 mg, 3.50 mmol) was separately added every 5 minutes six times. It was heated up to 100 °C and kept the temperature. To promote the reaction, 427 mg (3.09 mmol) and 284 mg (2.05 mmol) of K_2CO_3 were added after 3.5 hours and 6.0 hours, respectively. After more 2.0 hours, the reaction mixture was cooled down to rt and extracted with chloroform. The organic layer was washed with water, dried over Na_2SO_4 and evaporated in vacuum. The residue was purified by column chromatography (silica gel, dichloromethane, $R_f = 0.55$) to obtain 57.4 mg of pale yellow solid. Yield = 28.5%, m.p. 197 °C. I.R. (KBr, cm^{-1}): 2237(-CN). 1H NMR($CDCl_3$, TMS): $\delta = 7.79$ (s, 2H, Ar), 7.58(t, $J=9.10$ Hz, 2H, Ar), 7.02(d, $J=8.09$ Hz, 2H, Ar), 6.69(d, $J=8.08$ Hz, 2H, Ar).

$[3-PyO(m-Cl)]_2FN$ (**3b**)

A mixture of 4,5-dichlorophthalonitrile(103 mg, 0.523 mmol), 3-chloro-5-pyridine (**3-PyOH(m-Cl)**): 275 mg, 2.12 mmol), dry-DMSO(5 ml) was stirred at 60 °C under a nitrogen atmosphere for 10 min. To the reaction mixture, one sixth of K_2CO_3 (484 mg, 3.50 mmol) was separately added every 5 minutes six times. It was heated up to 100 °C and kept the temperature. To promote the reaction, 108 mg (0.776 mmol) of K_2CO_3 was added after 45 minutes. After more 45 minutes, the reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over

Na₂SO₄ and evaporated in vacuum. The residue was purified by column chromatography (silica gel, dichloromethane: ethyl acetate = 8 : 2(v/v), R_f = 0.47) to obtain 177.3 mg of pale yellow solid. Yield = 88.7%, m.p. 179 °C. I.R. (KBr, cm⁻¹): 2237(-CN). ¹H NMR(CDCl₃, TMS): δ = 8.45(d, J=5.81Hz, 2H, Ar), 8.22(d, J=9.3Hz, 2H, Ar), 7.32(s, 2H, Ar), 7.31-7.29 (m, 2H, Ar).

[4-PyO(m-Cl)]₂FN (3c)

A mixture of 4, 5-dichlorophthalonitrile(128 mg, 0.661 mmol), 2-chloro-4-hydroxypyridine (**4-PyOH(m-Cl)**): 339 mg, 1.95 mmol), dry- DMSO(5 ml) was stirred at 60 °C under a nitrogen atmosphere for 10 min. To the reaction mixture, a sixth part of K₂CO₃(1926 mg, 13.9 mmol) was separately added every 5 minutes six times. It was heated up to 100 °C and kept the temperature for 9 hours. The reaction mixture was cooled down to rt, extracted with chloroform and washed with water. The organic layer was dried over Na₂SO₄ and evaporated in vacuum. The residue was purified by column chromatography (silica gel, dichloromethane : ethyl acetate = 9 : 1(v/v), R_f = 0.67) to obtain 83.9 mg of pale yellow solid. Yield = 33.1%, m.p. 154 °C. I.R. (KBr, cm⁻¹): 2235(-CN). ¹H NMR(CDCl₃, TMS): δ = 8.40(d, J=7.83Hz, 2H, Ar), 7.63(s, 2H, Ar), 6.84 (d, J=2.27Hz, 2H, Ar), 6.78(dd, J₁=6.31, J₂=2.15, 2H, Ar).

[2-PyO(m-Cl)]₈PcCu (2a)

A mixture of **[2-PyO(m-Cl)]₂FN (3a)**: 91.0 mg, 0.237 mmol), CuCl₂(27.1 mg, 0.201 mmol), 1-hexanol (5 ml), DBU(3 drops) was refluxed under a nitrogen atmosphere for 4 h. After cooling to rt, methanol was poured into the reaction mixture to precipitate the target compound. The precipitates were collected by filtration and the filtrate was washed with methanol, ethanol and acetone, successively. The residue was resolved in a small amount of mixed solvents, chloroform : THF = 1:1(v/v). The solution was poured into a column for the column chromatography (silica gel). The impurities were removed by using the first eluent of chloroform and then the target Pc complex **2a** (R_f = 0.0 for chloroform) was collected by using the second eluent of THF. After evaporation of the solvent, the residue was purified by Soxhlet extraction using dry THF. The filtrate was evaporated and dried in vacuo to obtain 18.5 mg of green powder. Yield and MALDI-TOF Mass data: See Table 1. UV-vis spectral data: See Table 2. Phase transition behaviour: See Table 3.

[3-PyO(m-Cl)]₈PcCu (2b)

A mixture of **[3-PyO(m-Cl)]₂FN (3b)**: 70.9 mg, 0.185 mmol), CuCl₂(40.3 mg, 0.230 mmol), 1-hexanol (5 ml), DBU(3 drops) was refluxed under a nitrogen atmosphere for 6 h. After cooling to rt, methanol was poured into the reaction mixture to precipitate the target compound. The precipitates were collected by filtration and the filtrate was washed with methanol, ethanol and acetone, successively. The residue was resolved in a small amount of mixed solvents, chloroform : THF = 1:1(v/v). The solution was poured into a column for the column chromatography (silica gel). The impurities were removed by using the eluent of chloroform. Differently from **2a**, the target Pc complex **2b** (R_f = 0.0 for chloroform) was so tightly adhered to the silica gel that we could not remove it even by using THF. Therefore, the silica gel absorbed the Pc complex was poured into a big beaker and THF warmed at 60 °C was into the beaker with stirring. The resulted hot THF solution was collected by decantation. It was repeated 8 times. The combined THF solutions were evaporated to dryness. The residue was purified by Soxhlet extraction using dry THF. The filtrate was evaporated and dried in vacuo to obtain 14.1 mg of green powder. Yield and MALDI-TOF Mass data: See Table 1. UV-vis spectral data: See Table 2. Phase transition behaviour: See Table 3.

[4-PyO(m-Cl)]₈PcCu (2c)

A mixture of **[4-PyO(m-Cl)]₂FN (3c)**: 81.5 mg, 0.213 mmol), CuCl₂(27.6 mg, 0.205 mmol), 1-hexanol (5 ml), DBU(3drops) was refluxed under a nitrogen atmosphere for 3 h. After cooling to rt, methanol was poured into the reaction mixture to precipitate the target compound. The precipitates were collected by filtration and the filtrate was washed with methanol, ethanol and acetone, successively. The residue was resolved in a small amount of mixed solvents, chloroform : THF = 1:1(v/v). The solution was poured into a column for the column chromatography (silica gel). The

impurities were removed by using the first eluent of chloroform and the target Pc complex **2c** ($R_f = 0.0$ for chloroform) was collected by using the second eluent of THF. After evaporation of the solvent, the residue was purified by Soxhlet extraction using dry THF. The filtrate was evaporated and dried in vacuo to obtain 12.3 mg of green powder. Yield and MALDI-TOF Mass data: See Table 1. UV-vis spectral data: See Table 2. Phase transition behaviour: See Table 3.

Measurements

The compounds $[\mathbf{x-PyO}(m\text{-Cl})]_2\text{FN}$ (**3a-c**) synthesized here were identified with an FT-IR spectrometer (Nicolet NEXUS 670) and $^1\text{H-NMR}$ spectrometer (BRUKER Ultrashield 400 M Hz). The MALDI-TOF mass spectral measurements of phthalocyanine derivatives $[\mathbf{x-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2a-c**) were carried out by using a Bruker Daltonics Autoflex III spectrometer (matrix: dithranol). Electronic absorption (UV-vis) spectra of **2a** and **2c** were recorded by using a Hitachi U-4100 spectrophotometer. Phase transition behaviour of **2a-c** was observed with a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP-90 Central Processor, and a Shimadzu DSC-50 differential scanning calorimeter. The decomposition temperatures were measured by a Rigaku Thermo plus TG 820 thermogravimetry analyzer. The mesophases were identified by using a small angle X-ray diffractometer (Bruker Mac SAXS System) equipped with a temperature-variable sample holder with 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

Synthesis

Scheme 1 shows the synthetic route. The Pc compounds synthesized here were characterized by using MALDI-TOF mass spectra (Table 1) and UV-vis spectra (Table 2). However, one of these three derivatives, $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2b**), was hardly soluble in any solvents that the UV-vis spectrum could not be measured. Also these three Pc derivatives, **2a-c**, are much less flammable so that the elemental analyses were not carried out. However, it could be confirmed from their MALDI-TOF mass spectra and UV-vis spectra that the target derivatives, **2a-c**, were surely synthesized.

Phase transition behaviour

Phase transitions of the present derivatives $[\mathbf{x-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2a-c**) are summarized in Table 3. The mesomorphism was established by polarizing microscopic observations, DSC, TG-DTA and small angle X-ray diffraction measurements.

As can be seen from this table, the freshly prepared sample of $[\mathbf{2-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2a**) at rt shows a mixture of glassy tetragonal ordered columnar ($\text{Col}_{\text{tet},o}$) mesophase and a small amount of crystalline (K) phase. When the mixture of glassy $\text{Col}_{\text{tet},o}$ and K was heated from rt, a glass transition was observed at *ca.* 172 °C and then the resulted supercooled $\text{Col}_{\text{tet},o}$ mesophase relaxed into the crystalline phase K at 218 °C. On further heating, the crystalline phase K melted into a rectangular ordered columnar ($\text{Col}_{\text{ro1}}(\text{P2m})$) mesophase at 325 °C. The $\text{Col}_{\text{ro1}}(\text{P2m})$ mesophase transformed into another rectangular ordered columnar ($\text{Col}_{\text{ro2}}(\text{P2m})$) mesophase at 371 °C accompanied with gradual decomposition. On the other hand, the derivative $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2b**) showed a crystalline K phase from rt to the decomposition temperature of 248 °C without showing any mesophase. On the contrary, the derivative $[\mathbf{4-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2c**) showed a rectangular ordered columnar ($\text{Col}_{\text{ro1}}(\text{P2m})$) mesophase even at rt. When it was heated from rt, the $\text{Col}_{\text{ro1}}(\text{P2m})$ mesophase transformed into another rectangular ordered columnar ($\text{Col}_{\text{ro2}}(\text{P2m})$) mesophase at 306 °C accompanied with gradual decomposition.

Thus, the mesomorphism appeared with strong dependence of the position of nitrogen atom in *m*-chloropyridyloxy group. The derivative [2-PyO(*m*-Cl)]₈PcCu (2a) introduced a nitrogen atom at the 2-position shows mesomorphism only at very high temperatures over 325 °C. The derivative [4-PyO(*m*-Cl)]₈PcCu (2c) introduced a nitrogen atom at the 4-position shows mesomorphism in a very wide temperature region from rt to the decomposition temperature at 306 °C. On the other hand, the derivative [3-PyO(*m*-Cl)]₈PcCu (2b) introduced a nitrogen atom at the 3-position is not mesogenic but crystalline.

Polarizing microscopic observations

Figure 2 shows photomicrographs of the Pc derivatives, [x-PyO(*m*-Cl)]₈PcCu (2a-c). The photomicrographs (a) and (b) show the Col_{ro1}(P2m) mesophase at 350 °C and the Col_{ro2}(P2m) mesophase at 375 °C for the derivative [2-PyO(*m*-Cl)]₈PcCu (2a), respectively. As can be seen from these photomicrographs, when the cover glass was pressed at both 350 °C and 375 °C, the derivative 2a was spread to show stickiness together with birefringence between crossed Nicols. This means that these phases of Col_{ro1} and Col_{ro2} are mesomorphic.

The photomicrograph (c) shows the rigid crystals K of [3-PyO(*m*-Cl)]₈PcCu (2b) at rt. When the cover glass was pressed, this derivative showed rigidity in a whole temperature region from rt to 248 °C.

The photomicrographs (d) and (e) show the Col_{ro1}(P2m) mesophase at rt and the Col_{ro2}(P2m) mesophase at 340 °C for the derivative [4-PyO(*m*-Cl)]₈PcCu (2c), respectively. As can be seen from these photomicrographs, when the cover glass was pressed at both rt and 340 °C, the derivative [4-PyO(*m*-Cl)]₈PcCu (2c) was spread to show stickiness together with birefringence between crossed Nicols. This implies that these phases of Col_{ro1} and Col_{ro2} are mesomorphic. The derivatives 2a and 2c decompose without clearing into isotropic liquid (I.L.), so that their natural textures could not be obtained from the I.L. However, these mesophases could be confirmed from the stickiness with birefringence, as mentioned above.

Temperature-dependent X-ray diffraction measurements

In order to reveal the detailed mesophase structures, temperature-dependent small angle X-ray diffraction measurements were carried out for the mesogenic derivatives, [2-PyO(*m*-Cl)]₈PcCu (2a) and [4-PyO(*m*-Cl)]₈PcCu (2c). These X-ray diffraction (XRD) patterns and their X-ray data are summarized in Figures 3, 4 and Table 4, respectively.

As can be seen from Figure 3(A), the mesophase at rt in the derivative [2-PyO(*m*-Cl)]₈PcCu (2a) gave eleven sharp peaks. As can be seen from Table 4, all the peaks except for No. 3 and No. 7 could be well assigned to the reflections from a 2D tetragonal lattice having the lattice constant, $a = 21.4 \text{ \AA}$. Peak No. 7 could be assigned to the reflection corresponding to the stacking distance ($h = 5.54 \text{ \AA}$) in the intracolumnar disks. Therefore, this phase could be tentatively identified as a tetragonal ordered columnar (Col_{tet.o}) mesophase, but this phase was rigid when it was pressed on the cover glass at rt. Moreover, Peak No. 3 could not be assigned to any reflections from the 2D tetragonal lattice. It may be a peak from a 3D crystalline lattice. Hence, this state at rt was identified as a mixture states of a glassy Col_{tet.o} mesophase and small amount of a crystalline K phase.

As can be seen from Figure 3 [B], this derivative 2a at 350 °C gave eleven sharp peaks. All the peaks except for No. 7 could be well assigned to the reflections from a 2D rectangular (P2m) lattice having the lattice constants, $a = 20.7 \text{ \AA}$ and $b = 14.2 \text{ \AA}$, as can be seen from Table 4. Peak No. 7 could be assigned to the reflection corresponding to the stacking distance ($h = 5.15 \text{ \AA}$) of intracolumnar disks. Therefore, this mesophase could be identified as a Col_{ro1}(P2m) mesophase. As can be seen from Figure 3 [C], this derivative 2a at 375 °C gave eleven sharp peaks. All the peaks except for No. 7 could be well assigned to the reflections from a 2D rectangular (P2m) lattice having the lattice constants, $a = 20.0 \text{ \AA}$ and

$b = 14.2 \text{ \AA}$. Peak No. 7 was assigned to the reflection corresponding to the stacking distance ($h = 5.26 \text{ \AA}$) of intracolumnar disks. Therefore, this mesophase was also identified as another $\text{Col}_{\text{ro2}}(\text{P2m})$ mesophase.

Figure 4(A) and (B) show the X-ray diffraction patterns of the derivative $[\mathbf{4-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2c})$ at $150 \text{ }^\circ\text{C}$ and $340 \text{ }^\circ\text{C}$, respectively. In the same manner above-mentioned for $\mathbf{2a}$, the mesophases in $\mathbf{2c}$ at $150 \text{ }^\circ\text{C}$ and $340 \text{ }^\circ\text{C}$ could be also identified as a rectangular ordered columnar mesophase $\text{Col}_{\text{ro1}}(\text{P2m})$ having the lattice constants, $a = 19.6 \text{ \AA}$, $b = 16.0 \text{ \AA}$ and $h = 4.42 \text{ \AA}$, and another rectangular ordered columnar mesophase $\text{Col}_{\text{ro2}}(\text{P2m})$ having the lattice constants, $a = 19.5 \text{ \AA}$, $b = 16.0 \text{ \AA}$ and $h = 4.51 \text{ \AA}$, respectively. These X-ray data are listed up also in Table 4.

Relationship between mesomorphism and position of the nitrogen atom in pyridyloxy group

As mentioned above, $[\mathbf{2-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2a})$ and $[\mathbf{4-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2c})$ show mesomorphism but $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2b})$ does not show it.

Figure 5 illustrates molecular structures of all the octakis(*m*-chloropyridyloxyphthalocyanato) copper(II) complexes, $[\mathbf{x-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2a-c})$. Only the nitrogen atom in the $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2b})$ derivative can be close to the neighbouring chlorine atom by rotation, so that an additional intramolecular N...Cl halogen bond may be formed in the nearest *m*-chloropyridyloxy groups.¹³ Hence, the *m*-chloropyridyloxy groups fixed by the halogen bond may neither rotate nor flip-flop to form the soft parts essential for mesomorphism.¹⁻⁶ Therefore, the derivative $\mathbf{2b}$ cannot show mesomorphism. Moreover, it is very interesting that the derivative $[\mathbf{2-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2a})$ shows mesomorphism only at very high temperatures over $325 \text{ }^\circ\text{C}$, whereas the derivative $[\mathbf{4-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2c})$ shows mesomorphism in a very wide temperature region from rt to the decomposition temperature at $306 \text{ }^\circ\text{C}$. It may be attributed to the intermolecular N...Cl halogen bond that $\mathbf{2a}$ can form but $\mathbf{2c}$ cannot. In the very high temperature region, the intermolecular N...Cl halogen bond of $\mathbf{2a}$ may be destroyed to start the rotation or flip-flop of the *m*-chloropyridyloxy groups. Therefore, the derivative $\mathbf{2a}$ shows mesomorphism only at very high temperatures over $325 \text{ }^\circ\text{C}$. On the other hand, the derivative $\mathbf{2c}$ may form neither intramolecular nor intermolecular halogen bonds, so that derivative $\mathbf{2c}$ shows mesomorphism in a very wide temperature region from rt to the decomposition temperature at $306 \text{ }^\circ\text{C}$.

Thus, both intramolecular and intermolecular halogen bonds may more or less prevent inducing mesomorphism for the present octakis(*m*-chloropyridyloxy)phthalocyaninato copper(II) complexes. On the contrary, halogen bonds in all the liquid crystals reported to date promote to induce mesomorphism.¹⁴⁻²⁸

CONCLUSION

In this study, we have synthesized novel octakis(*m*-chloropyridyloxy)phthalocyaninato copper(II) complexes, $[\mathbf{x-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{x} = 2, 3, 4; \mathbf{2a-c})$, keeping a chlorine atom at the *meta* position on the 2-, 3- and 4-pyridyloxy group, in which the nitrogen atom is located at the 2-, 3- and 4-positions, respectively, and investigated the influence of the position of nitrogen atom in the *m*-chloropyridyloxy group on their mesomorphism.

As a result, the derivative $[\mathbf{2-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2a})$ introduced a nitrogen atom at the 2-position shows columnar mesomorphism only at very high temperatures over $325 \text{ }^\circ\text{C}$. The derivative $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2b})$ introduced a nitrogen atom at the 3-position is not mesogenic but crystalline. On the other hand, the derivative $[\mathbf{4-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2c})$ introduced a nitrogen atom at the 4-position shows columnar mesomorphism in a very wide temperature region from rt to the decomposition temperature at $306 \text{ }^\circ\text{C}$. Thus, the mesomorphism appears with strong dependence of the position of nitrogen in *m*-chloropyridyloxy group.

We have discussed about relationship between their mesomorphism and the position of nitrogen atom in *m*-chloropyridyloxy group. The $[\mathbf{3-PyO}(m\text{-Cl})]_8\text{PcCu}(\mathbf{2b})$ derivative may form an additional intramolecular N...Cl

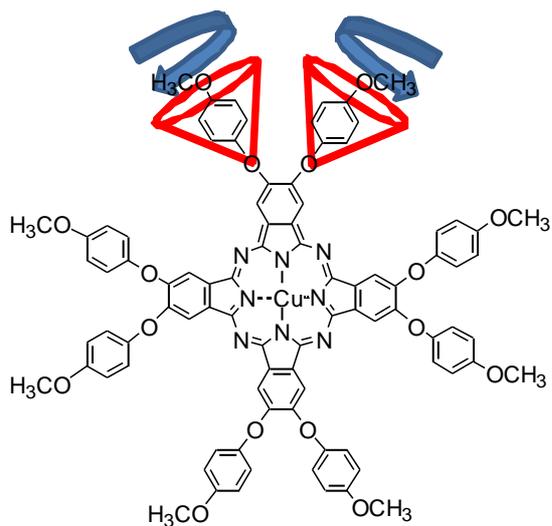
halogen bond in the nearest *m*-chloropyridyloxy groups. Hence, the *m*-chloropyridyloxy groups fixed by the halogen bond may neither rotate nor flip-flop to prevent showing mesomorphism. The derivative [2-PyO(*m*-Cl)]₈PcCu (2a) can form the intermolecular N...Cl halogen bond at lower temperatures, but the halogen bond may be destroyed at very high temperatures over 325 °C to show mesomorphism. On the other hand, the derivative [4-PyO(*m*-Cl)]₈PcCu (2c) may form neither intramolecular nor intermolecular N...Cl halogen bond, so that it shows mesomorphism in a very wide temperature region from rt to 306 °C. Thus, appearance of the mesomorphism in the present [x-PyO(*m*-Cl)]₈PcCu (2a-c) derivatives strongly depends on the position of nitrogen atom in *m*-chloropyridyloxy group and it can be explained from the viewpoint of halogen bond.

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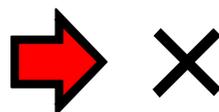
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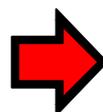
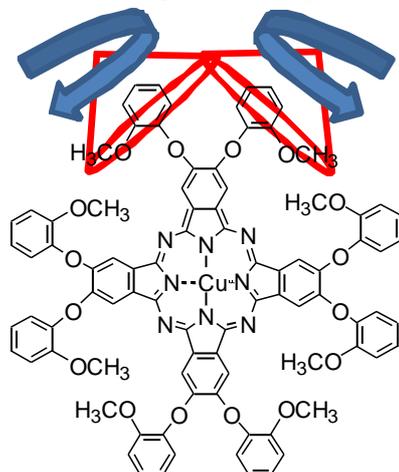
1a: [(*p*-C₁)PhO]₈PcCu



Appearance of mesomorphism



1b: [(*o*-C₁)PhO]₈PcCu



(Monotropic)

1c: [(*m*-C₁)PhO]₈PcCu

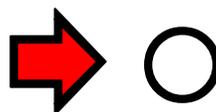
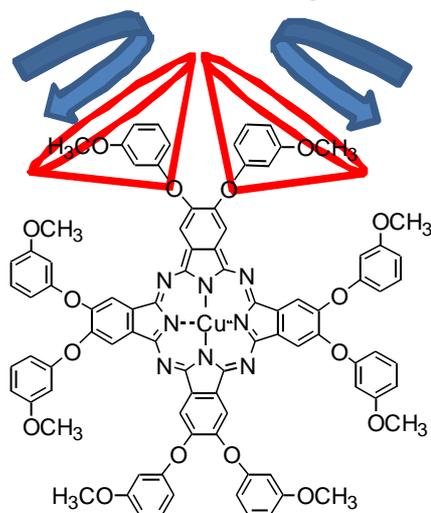
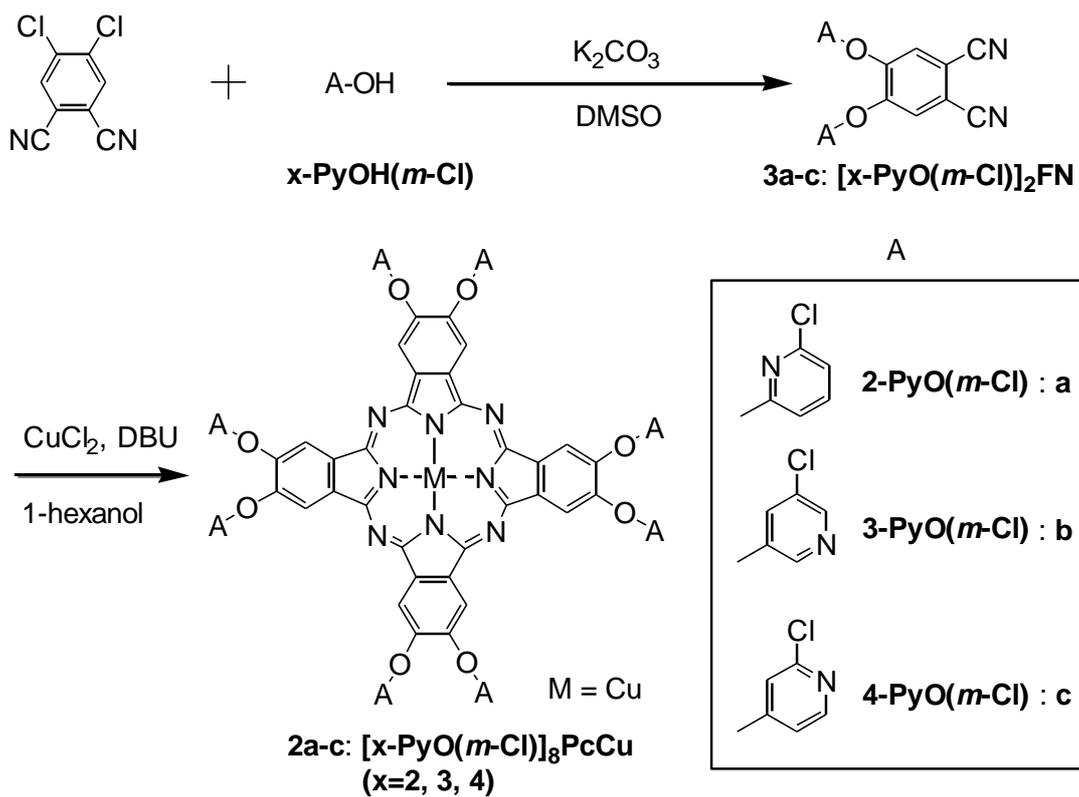


Figure 1. Appearance of mesomorphism depending on the position of methoxy groups for [(*x*-C₁)PhO]₈PcCu (*x* = *p*, *o*, *m* : **1a-c**). ×: no mesophase appears; △ : monotropic mesophase appears; ○: enantiotropic mesophase appears.



Scheme 1. Synthetic route for $[x-PyO(m-Cl)]_8PcCu(2a-c)$. DMSO = dimethyl sulfoxide and DBU = 1,8-diazabicyclo[5, 4, 0] undec-7-ene.

Table 1. Yields and MALDI-TOF mass spectral data of [(x-PyO(m-Cl))₈PcCu: 2a-c.

Compound	Yield (%)	Mol. formula (Average Mass) Exact Mass	Observed Exact Mass
2a: [2-PyO(m-Cl)]₈PcCu	19.5	C ₇₂ H ₃₂ Cl ₈ CuN ₁₆ O ₈ (1596.30) 1590.94	1591.87(M+1)
2b: [3-PyO(m-Cl)]₈PcCu	19.1	C ₇₂ H ₃₂ Cl ₈ CuN ₁₆ O ₈ (1596.30) 1590.94	1591.03
2c: [4-PyO(m-Cl)]₈PcCu	9.12	C ₇₂ H ₃₂ Cl ₈ CuN ₁₆ O ₈ (1596.30) 1590.94	1591.01

 Table 2. Electronic spectral data of [(x-PyO(m-Cl))₈PcCu: 2a-c.

Compound	Concentration [#] (X10 ⁻⁶ mol/l)	λ_{\max} (nm) (log ϵ)				
		Soret-band		Q-band		
2a: [2-PyO(m-Cl)]₈PcCu	4.96	274.4 (4.90)	348.1 (4.88)	609.4 (4.52)	634.3* (4.81)	672.6 (5.09)
2b: [3-PyO(m-Cl)]₈PcCu [§]	-	-	-	-	-	-
2c: [4-PyO(m-Cl)]₈PcCu	6.29	252.9 (4.28)	352.4 (4.38)	606.7 (4.04)	639.8* (4.13)	670.8 (4.44)

[#]: In THF. *: Aggregation band of Q₀₋₀. [§]: This derivative is insoluble in any solvents.

 Table 3. Phase transition temperatures of [(x-PyO(m-Cl))₈PcCu: 2a-c.

Compound	Phase	T (°C) [ΔH (kJmol ⁻¹)]	Phase	Relaxation
2a: [2-PyO(m-Cl)]₈PcCu	Glassy Col _{tet,o}	$T_g = ca. 172$	supercooled Col _{tet,o}	
			K	
2b: [3-PyO(m-Cl)]₈PcCu			K	ca. 248 → dc.
			Col _{ro1} (P2m)	306[16.3] → Col _{ro2} (P2m) (dc.)
2c: [4-PyO(m-Cl)]₈PcCu			Col _{ro1} (P2m)	306[16.3] → Col _{ro2} (P2m) (dc.)

Phase nomenclature: K = crystal, Col_{tet,o} = tetragonal ordered columnar mesophase, Col_{ro} = rectangular ordered columnar mesophase and dc. = decomposition.

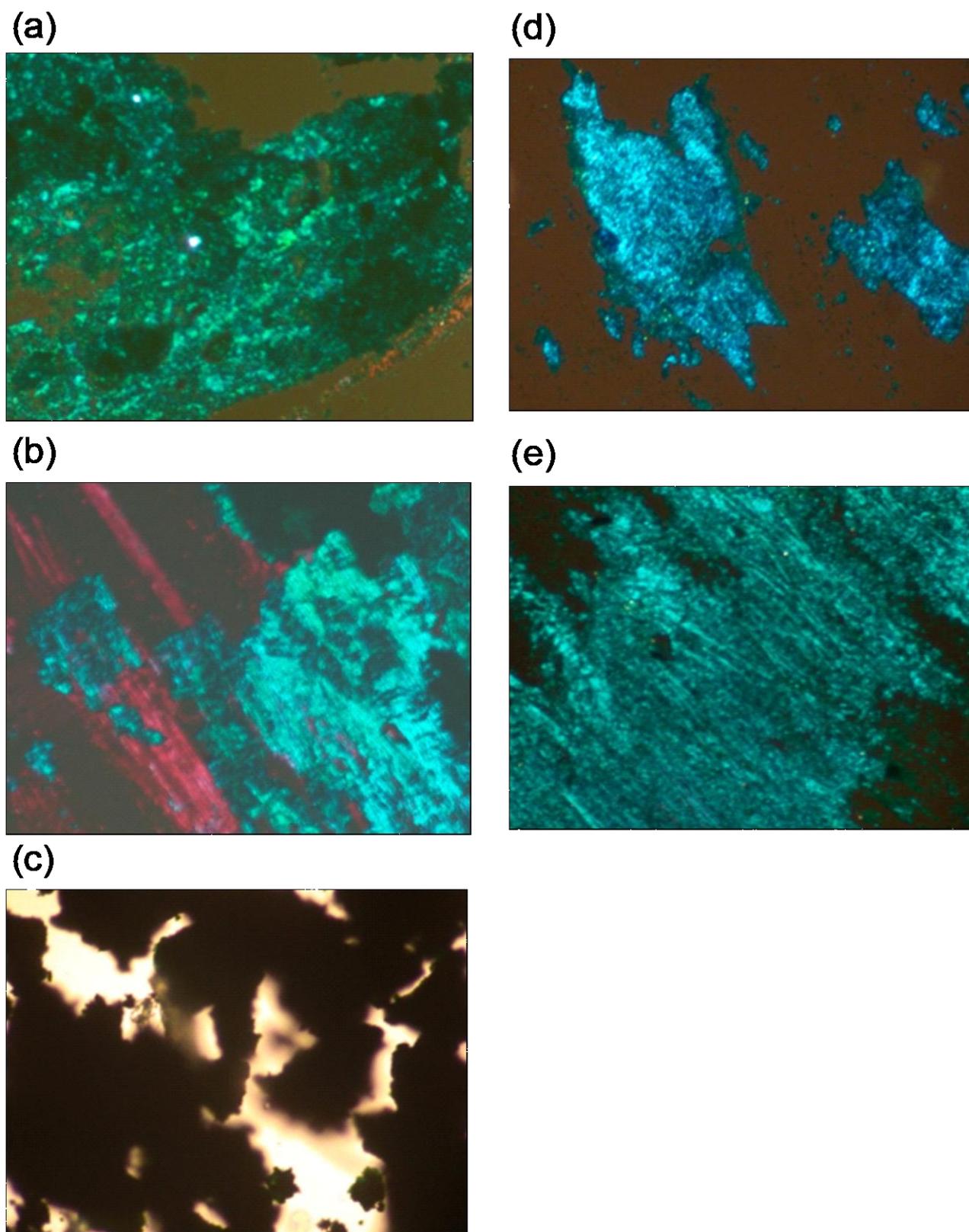


Figure 2. Photomicrographs. $[2\text{-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2a**); (a): $\text{Col}_{\text{r01}}(\text{P2m})$ at $350\text{ }^\circ\text{C}$; (b): $\text{Col}_{\text{r02}}(\text{P2m})$ at $375\text{ }^\circ\text{C}$. $[3\text{-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2b**); (c): K at rt. $[4\text{-PyO}(m\text{-Cl})]_8\text{PcCu}$ (**2c**); (d): $\text{Col}_{\text{r01}}(\text{P2m})$ at rt; (e): $\text{Col}_{\text{r02}}(\text{P2m})$ at $340\text{ }^\circ\text{C}$.

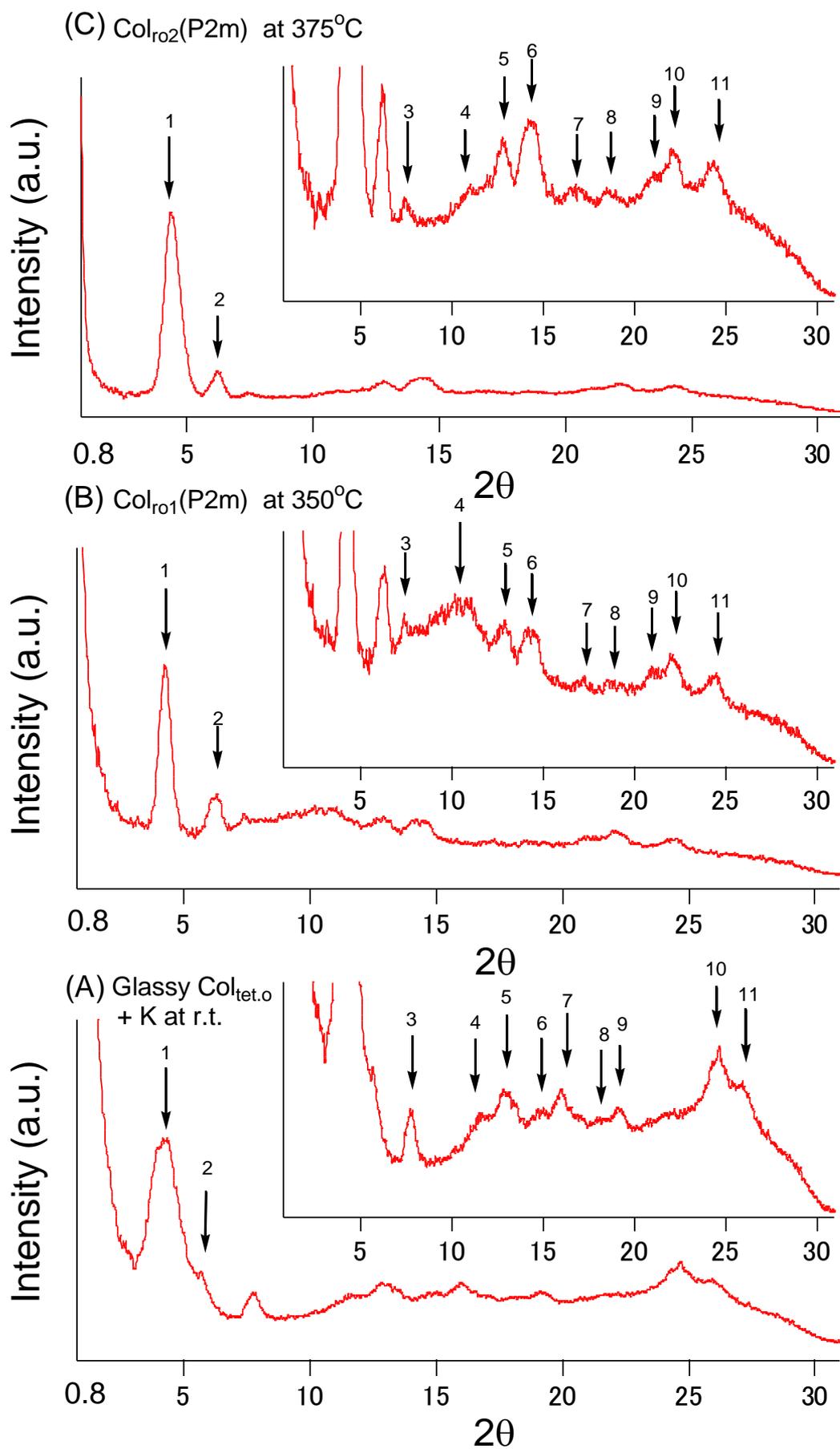
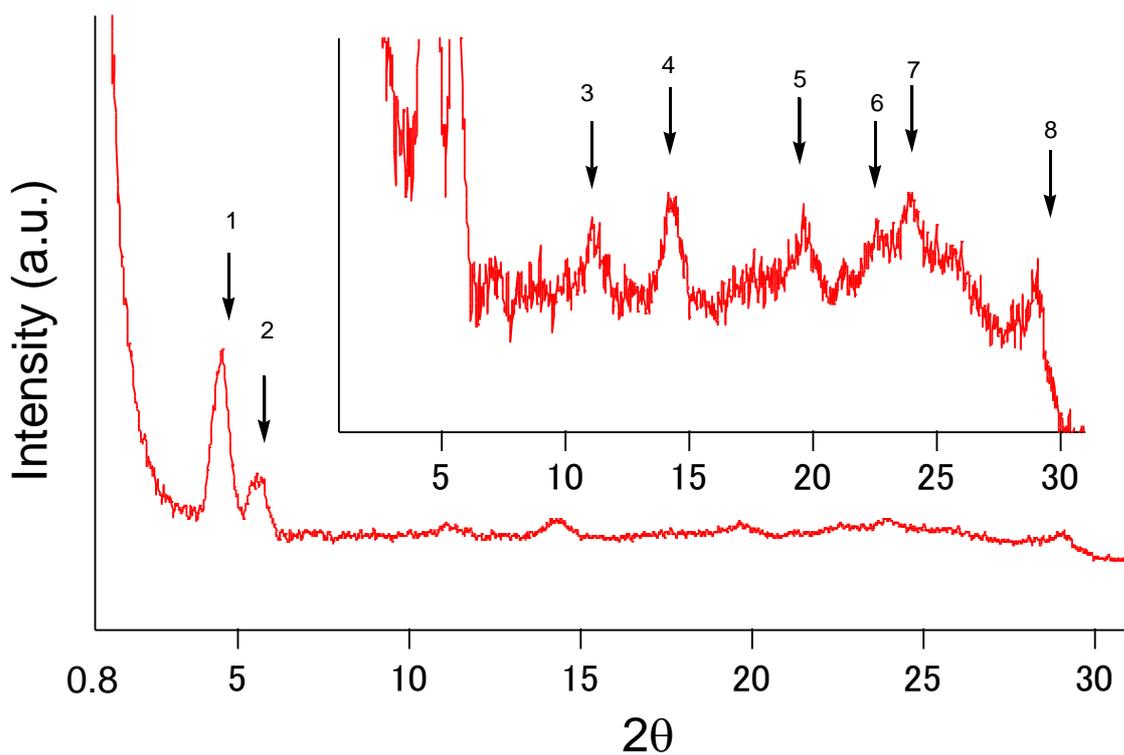


Figure 3. X-ray diffraction patterns of [2-PyO(*m*-Cl)]₈PcCu (**2a**) at rt, 350 °C and 375 °C.

(B) Col_{ro2}(P2m) at 340°C



(A) Col_{ro1}(P2m) at 150°C

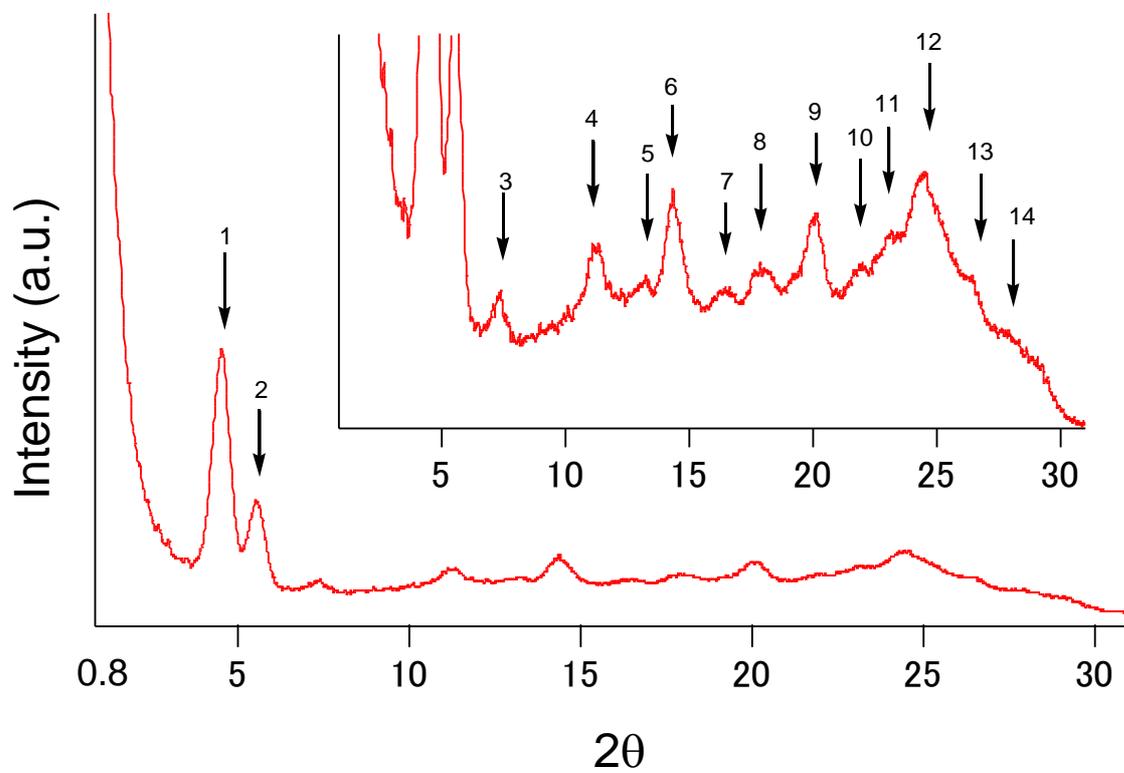


Figure 4. X-ray diffraction patterns of [4-PyO(*m*-Cl)]₈PcCu (2c): (A) at 150 °C and (B) at 340 °C.

Table 4. X-ray data of **2a** and **2c**.

Compound Mesophase lattice constants(Å)	Peak No.	Spacing(Å)		Miller indices (h k l)
		Observed	Calculated	
2a: [2-PyO(m-Cl)]₈PcCu tentatively assigned glassy Col _{tet.o} +K at r.t. a = 21.4 h = 5.54 Z = 1.0 for ρ = 1.8	1	21.1	21.1	(1 0 0)
	2	15.6	15.6	(1 1 0)
	3	11.4	-	X
	4	7.49	7.60	(2 2 0)
	5	6.81	6.73	(3 1 0)
	6	5.97	5.99	(2 3 0)
	7	5.54	5.54	h
	8	4.87	4.79	(4 2 0)
	9	4.62	4.56	(2 4 0)
	10	3.61	3.58	(0 6 0)
	11	3.45	3.45	(1 6 0)
Col _{ro1} (P2m) at 350 °C a = 20.7 b = 14.2 h = 5.15 Z = 1.0 for ρ = 1.8	1	20.7	20.7	(1 0 0)
	2	14.2	14.2	(0 1 0)
	3	12.0	11.7	(1 1 0)
	4	8.38	8.35	(2 1 0)
	5	6.88	6.90	(3 0 0)
	6	6.18	6.20	(3 1 0)
	7	5.14	5.14	h
	8	4.70	4.71	(0 3 0)
	9	4.19	4.17	(4 2 0)
	10	4.03	3.89	(3 3 0)
	11	3.65	3.53	(0 4 0)
Col _{ro2} (P2m) at 375 °C a = 20.0 b = 14.2 h = 5.26 Z = 1.0 for ρ = 1.8	1	20.0	20.0	(1 0 0)
	2	14.2	14.2	(0 1 0)
	3	11.9	11.6	(1 1 0)
	4	8.06	8.18	(2 1 0)
	5	6.92	7.09	(0 2 0)
	6	6.16	6.04	(3 1 0)
	7	5.26	5.26	h
	8	4.71	4.72	(4 1 0)
	9	4.19	4.27	(2 3 0)
	10	4.03	4.00	(5 0 0)
	11	3.66	3.54	(0 4 0)
2c: [4-PyO(m-Cl)]₈PcCu Col _{ro1} (P2m) at 150 °C a = 19.6 b = 16.0 h = 4.42 Z = 1.0 for ρ = 1.9	1	19.6	19.6	(1 0 0)
	2	16.0	16.0	(0 1 0)
	3	12.0	12.4	(1 1 0)
	4	7.89	8.00	(0 2 0)
	5	6.69	6.54	(3 0 0)
	6	6.16	6.20	(2 2 0)
	7	5.38	5.33	(0 3 0)
	8	4.96	4.91	(4 0 0)
	9	4.58	4.68	(2 3 0)
	10	4.42	4.42	h
	11	4.04	4.00	(0 4 0)
	12	3.80	3.81	(5 1 0)
	13	3.64	3.61	(4 3 0)
	14	3.41	3.41	(3 4 0)
Col _{ro2} (P2m) at 340 °C a = 19.5 b = 16.0 h = 4.51 Z = 1.0 for ρ = 1.9	1	19.5	19.5	(1 0 0)
	2	16.0	16.0	(0 1 0)
	3	7.97	8.01	(0 2 0)
	4	6.19	6.19	(2 2 0)
	5	4.51	4.51	h
	6	4.18	4.17	(4 2 0)
	7	3.71	3.70	(2 4 0)
	8	3.08	3.10	(4 4 0)

h: Stacking distance = (0 0 1), ρ: Assumed density (g/cm³), X= a reflection from 3D crystalline lattice.

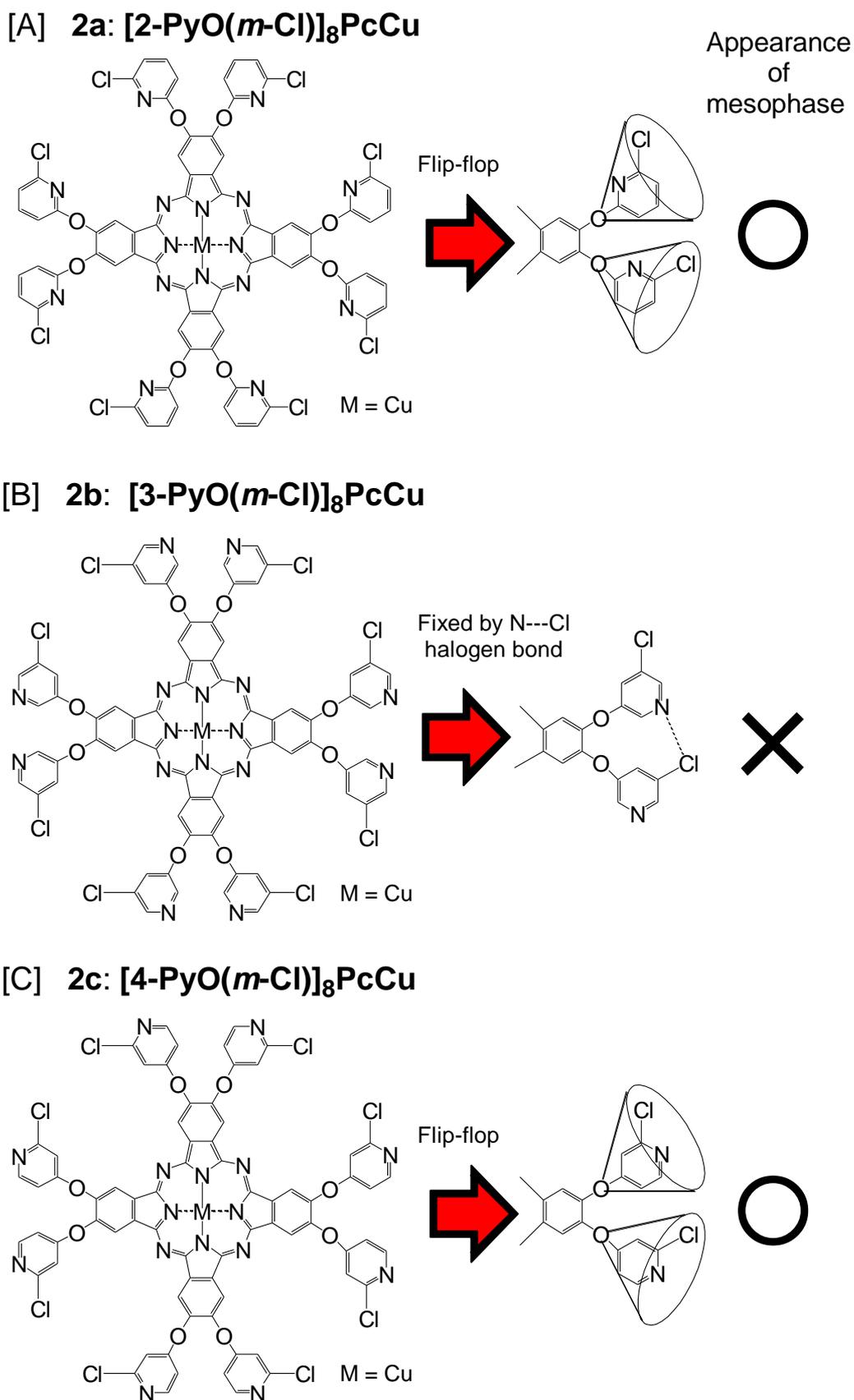


Figure 5. Appearance of the mesomorphism depending on both flip-flop of the bulky *m*-chloropyridyloxy groups and the N...Cl halogen bond. ×: no mesophase appears; ○: enantiotropic mesophase appears.