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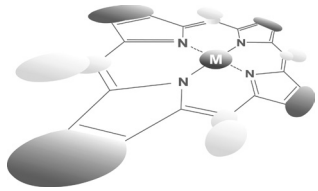

Discotic liquid crystals of transition metal complexes 46†: mesomorphism and antagonist solubility of octaphenoxy-phthalocyaninato copper(II) complex substituted by oligoether chains

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ABSTRACT: We synthesized a novel discotic liquid crystalline compound, octakis[3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenoxy]phthalocyaninato copper(II) (abbreviated as [*m*-MeO-$(EtO)_3PhO]_8$PcCu), and established the mesomorphism by using a differential scanning calorimeter, a polarizing optical microscope, and temperature-dependent wide angle X-ray diffraction diffractometer. Very interestingly, this [*m*-$MeO(EtO)_3PhO]_8$PcCu complex showed a hexagonal ordered columnar (Col_{ho}) mesophase in the virgin sample, whereas it showed a rectangular ordered columnar ($Col_{ro}(P2_1/a)$) mesophase in the non-virgin sample. The Col_{ho} mesophase gave a dimer stacking distance at 9.26 Å, whereas the Col_{ro} mesophase gave a short monomer stacking distance at 3.45 Å. Furthermore, this novel Pc derivative is readily soluble in polar solvents such as acetone, ethanol and methanol. Using antagonist solubilities of the present hydrophilic [*m*-$MeO(EtO)_3PhO]_8$PcCu derivative in a polar solvent and the previous hydrophobic $(C_{10}O)_{16}$TzCu derivative in the non-polar solvent, a p-n junction layered thin films could be successfully prepared.

KEYWORDS: discotic liquid crystal, antagonist solubility, phthalocyanine, columnar mesophase, p-n junction.

INTRODUCTION

Discotic liquid crystals have been investigated as self-organized soft materials. They generally consist of an aromatic core surrounded by several long chains to show mesomorphism [1, 2]. Many discotic liquid crystals have been synthesized for different core systems. Especially, triphenylene-based derivatives [3] and phthalocyanine-based ones [4] have been studied intensively to date. Discotic liquid crystals form columnar mesophases by piling up the aromatic core parts by the π–π interactions. The one-dimensional columnar structures can allow fast charge carrier transportation along the columns [5–7]. Hence, we have been focused our interests on discotic liquid crystalline semiconductors and their applications to solar cells [8, 9], electroluminescent displays [10, 11], and field effect transistors [12, 13]. Performance of such electronic devices may be largely influenced by the stacking distance in the columnar mesophases [16, 17].

Currently, organic thin films for solar cells are formed by vacuum deposition method [18, 19]. This is due to low solubilities of the conventional organic semiconductors in organic solvents, which limit the film formation methods. If liquid crystalline semiconductors would be

◊SPP full member in good standing

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employed, the solubilities would be greatly improved and the film formation could be achieved, for example by spin coating. These film formation methods enable us to reduce the cost and easily form large area of thin films. Moreover, when discotic liquid crystalline donor (p-type) and acceptor (n-type) semiconductors are employed, they spontaneously form a one-dimensional columnar structure, which forms an excellent pathway for hole and electron transport. Generally, when liquid crystalline compounds are substituted by **hydrophobic** alkyl and alkoxy groups, they become readily soluble in non-polar solvents. On the other hand, when liquid crystalline compounds are substituted by **hydrophilic** oligoether and hydroxy groups, they become to be readily soluble in polar solvents, instead. Therefore, these two types of liquid crystalline compounds can show antagonist solubilities. Antagonist solubility means that one compound is soluble in a solvent but another compound is insoluble in the same solvent. Antagonist solubility can make the device fabrication very easy [20]. When both n-type and p-type of liquid crystalline semiconductors could be given such antagonist solubilities, the p-n junction of two layered thin films could be easily prepared by spin coating, casting and so on.

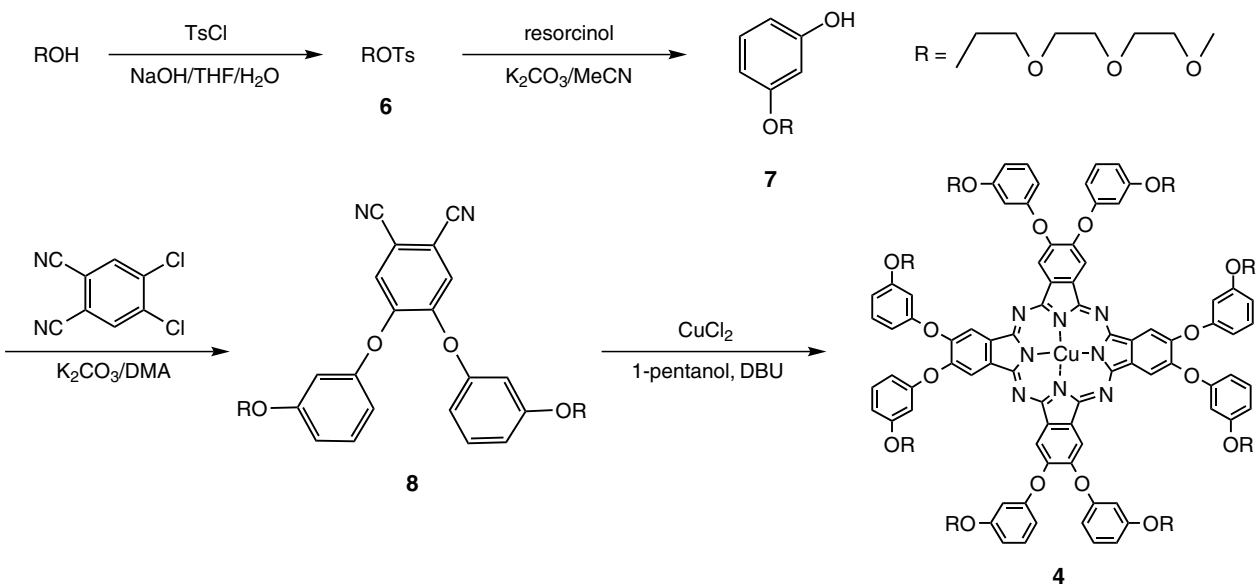
We have investigated many columnar liquid crystals based on phthalocyanine to date. Among them, we found very fast carrier mobilities, 0.28 cm^2/Vs for 2,3,9,10,16,17,23,24-oct-akis(alkylthio)phthalocyanine (abbreviated as $(C_{12}S)_8PcH_2$: **1**) [21], and 0.71 cm^2/Vs for bis[2,3,9,10,16,17,23,24-octakis(alkylthio)phthalocyaninato]lutetium(III) (abbreviated as $[(C_{12}S)_8Pc]_2Lu$: **2**) [17]. We also synthesized 2,3,9,10,16,17,23,24-octakis(3-dodecyloxyphenoxy)phthalocyaninato copper(II) (abbreviated as $(m\text{-}C_{12}OPhO)_8PcCu$: **3**) as a p-type of liquid crystalline semiconductor [22]. It shows a single columnar mesophase having a very short stacking distance 3.33 Å. Such a short stacking distance may afford very fast carrier mobility. Since this $(m\text{-}C_{12}OPhO)_8PcCu$ (**3**) derivative is substituted by the **hydrophobic** alkoxy groups, it is insoluble in polar solvent such as acetone, ethanol and so on. Accordingly, in this work we have synthesized a novel phthalocyanine derivative substituted by **hydrophilic** oligoether groups, 2,3,9,10,16,17,23,24-octakis[3-(2-(2-(2-methoxyethoxy) ethoxy)ethoxy)phenoxy]phthalocyaninato copper(II) (abbreviated as $[m\text{-}MeO(EtO)_3PhO]_8PcCu$: **4**). We expected this new Pc derivative would give a single columnar mesophase having a very short stacking distance and good solubility in polar solvents. If successful, the obtained hydrophilic p-type liquid crystalline $[m\text{-}MeO(EtO)_3PhO]$ (**4**) derivative will be able to form a thin film on a thin film of the previously synthesized hydrophobic n-type liquid crystalline derivative, tetrakis(2,3,6,7-tetraalkoxy)-1,4-diazatriphenylenocyaninato copper(II) (abbreviated as $(C_nO)_{16}TzCu$: **5**) [23], and prepare a p-n junction of the layered films by using their antagonist solubilities.

We wish to report here the synthesis and interesting properties of the novel $[m\text{-}MeO(EtO)_3PhO]_8PcCu$ (**4**) derivative. The formation of a double layer film of **4** and **5** is also described.

EXPERIMENTAL

Synthesis

Scheme 1 shows the synthetic route for the phthalocyanine copper complex ($[m\text{-}MeO(EtO)_3PhO]_8PcCu$ (**4**)). The starting materials of triethylene glycol monomethyl ether and *p*-toluenesulfonyl chloride (TsCl) were purchased from Tokyo Chemical Industry (Tokyo Kasei) and



Scheme 1. Synthetic route for $[m\text{-}MeO(EtO)_3PhO]_8PcCu$ (**4**). DMA = *N*, *N*′-dimethylacetamide and DBU = 1, 8-diazabicyclo[5, 4, 0]-7-undecene and TsCl = p-toluenesulfonyl chloride and THF = tetrahydrofuran

Kanto Chemical Co., Inc. (Kanto Kagaku), respectively. Ether derivative **6** was synthesized from triethylene glycol monomethyl ether and TsCl by the method of Percec *et al.* [24]. Phenol derivative **7** was synthesized from commercially available resorcinol (Wako Pure Chemical Industry: Wako) and the ether derivative **6** by the method of Dennis *et al.* [25]. Dicyano derivative **8** was synthesized from commercially available 4, 5-dichlorophthalonitrile (Tokyo Kasei) and the ether derivative **6** by our previously reported method [22]. The target phthalocyanine derivative **4** was synthesized from the dicyano derivative **8**. The detailed procedures are described as follows.

2-[2-(2-methoxyethoxy)ethoxy]ethoxy-1-(4-methylbenzenesulfonate) (6). Into a 100 mL of three-necked flask, triethylene glycol monomethyl ether (5.42 g, 33.0 mmol), NaOH (2.0 g), tetrahydrofuran (THF) (30 mL) and water (5 mL) were poured. The flask was immersed in an ice-water bath. To this solution, a solution of TsCl (5.25 g, 27.5 mmol) in 7.5 mL of THF was added dropwise with keeping temperature of the reaction mixture < 5 °C. After complete addition, the reaction mixture was stirred at 0 °C for 2 h. After neutralization with 10% HCl aqueous solution, it was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, evaporated under reduced pressure and dried under vacuum to give 8.51 g of transparent oil. Yield 97%. ^{1}H NMR ($CDCl_3$, TMS): δ, ppm 2.45 (3H, s, Ph-C*H*$_3$), 3.37 (3H, s, O-C*H*$_3$), 3.51–3.70 (10H, m, O-C*H*$_2$-C*H*$_2$-O, SO_2OCH_2- C*H*$_2$-O), 4.16 (2H, t, *J* = 4.8 Hz, SO_2O-C*H*$_2$), 7.34 (2H, d, *J* = 8.6 Hz, Ph-*H*), 7.79 (2H, d, *J* = 8.4 Hz, Ph-*H*).

3-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]phenol (7). Into a 200 mL of three-necked flask, 2-[2-(2-methoxyethoxy)ethoxy]ethoxy-1-(4-methylbenzenesulfonate) (**6**: 8.53 g, 26.8 mmol), resorcinol (5.90 g, 53.6 mmol), K_2CO_3 (10 g) and acetonitrile (100 mL) were poured. It was refluxed with stirring under a nitrogen atmosphere for 24 h. After complete reaction, the suspension was filtered. The filtrate was concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate:n-hexane = 2:1 (v/v), R_f = 0.45). The product was obtained as yellow oil (2.43 g). Yield 35%. IR (KBr, cm^{-1}): 3240 (-OH), 2924, 2879 (-CH_2-), 2825 (-OCH_3). ^{1}H NMR (d_6-DMSO, TMS): δ, ppm 3.24 (3H, s, O-C*H*$_3$), 3.42–3.58 (8H, m, O-C*H*$_2$-C*H*$_2$-O), 3.70 (2H, t, *J* = 4.7 Hz, O-C*H*$_2$-C*H*$_2$-O), 3.99–4.02 (2H, m, PhO-C*H*$_2$), 6.31–6.37 (3H, m, Ph-*H*), 7.04 (1H, t, *J* = 8.1 Hz, Ph-*H*).

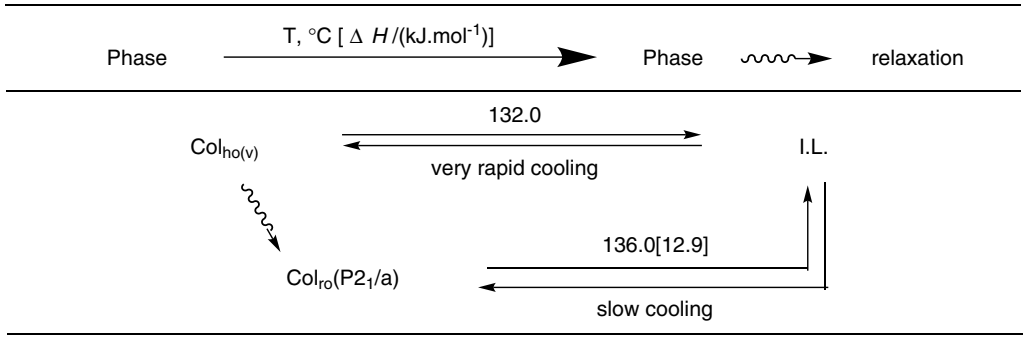
4,5-bis[3-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]-phenoxy]phthalonitrile (8). Into a 50 mL of three necked flask, 3-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]-phenol (**7**: 2.51 g, 9.48 mmol), 4, 5-dichlorophthalonitrile (0.778 g, 3.95 mmol), K_2CO_3 (8 g) and dry *N*, *N*′-dimethylacetamide (DMA: 22 mL) were poured. The reaction mixture was heated with stirring at 120 °C under a nitrogen atmosphere for 2 h. It was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate, R_f = 0.45). The product was obtained as pale yellow oil (1.31 g). Yield 52%. IR (KBr, cm^{-1}): 2924, 2875 (-CH_2-), 2814 (-OCH_3), 2232 (-CN). ^{1}H NMR ($CDCl_3$, TMS): δ, ppm 3.38 (6H, s, O-C*H*$_3$), 3.54–3.56 (4H, m, O-C*H*$_2$-C*H*$_2$-O), 3.64–3.75 (12H, m, O-C*H*$_2$-C*H*$_2$-O), 3.87 (4H, t, *J* = 4.9 Hz, $PhOCH_2$-C*H*$_2$), 4.11–4.15 (4H, m, PhO-C*H*$_2$), 6.64–6.65 (4H, m, Ph-*H*), 6.80–6.85 (2H, m, Ph-*H*), 7.20 (2H, s, Ph-*H*), 7.33 (2H, t, *J* = 8.6 Hz, Ph-*H*).

2,3,9,10,16,17,23,24-octakis[3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenoxy]- phthalocyaninato copper (II) (4). Into a 50 mL of three necked flask, 4, 5-bis [3-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]- phenoxy]phthalonitrile (**8**: 0.400 g, 0.628 mmol), 1-pentanol (4 mL), $CuCl_2$ (42.2 mg, 0.314 mmol) and 1, 8-diazabicyclo[5, 4, 0]-7-undecene (DBU: 5 drop) were poured. The reaction mixture was refluxed under a nitrogen atmosphere for 24 h. After complete reaction, it was evaporated under reduced pressure. The residue was purified by solid-liquid extraction with hot *n*-hexane. The remained product was further purified by column chromatography: the impurities were eluted with a mixture solvent of $CHCl_3$:THF = 2:1(v/v) (silica gel, except for Rf = 0) and the target compound at Rf = 0 was eluted with THF. The pure product was obtained as a dark green liquid crystal (0.383 g). Yield 93%. UV-vis ($CHCl_3$; concentration: 7.66 × 10^{-6} M): λ_{max} nm (log ε) 283.0 (4.91), 341.8 (4.98), 389.2 (4.66), 613.4 (4.72), 649.5 (4.68), 681.3 (5.45). MS (MALDI-TOF): *m/z* 2609.98 (calcd. 2610.30). Anal. calcd. For $C_{136}H_{160}N_8$: C, 62.33: H, 6.10: N, 4.29%. Found: C, 62.58; H, 6.18: N, 4.29%.

Measurements

The compounds synthesized here were identified with a ^{1}H NMR (BRUKER Ultrashield 400 M Hz), an elemental analyzer (Perkin-Elmer elemental analyzer 2400). The phase transition temperatures and enthalpy changes were measured with a differential scanning calorimeter (Shimadzu DSC-50). Electronic absorption apectra of the phthalocyanine derivative were recorded by using a HITACHI U-4100 spectrophotometer. The textures of their mesophases were observed with a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP90 Central Processor. Wide angle X-ray diffraction measurements were carried out with Cu-Kα radiation with a Rigaku RAD X-ray diffractometer equipped with a handmade heating plate [26] controlled with a thermoregulator.

Table 1. Phase transition temperatures and enthalpy change of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**)



Phase nomenclature: Col_{ho} = hexagonal ordered columnar mesophase, Col_{ro} = rectangular ordered columnar mesophase and I.L. = isotropic liquid. v = virgin state.

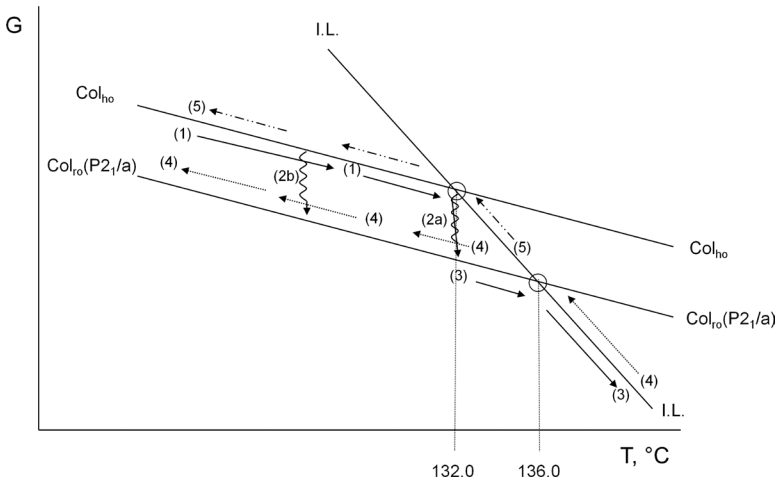


Fig. 1. Free energy vs. temperature (G-T) diagram for [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). The intersection temperatures are measured points, but the actual slopes are unknown. Step: (1) heating of Col_{ho} mesophase, (2) relaxation, (3) further heating over clearing point, (4) cooling, and (5) supercooling

RESULTS AND DISCUSSION

Phase transition behavior

Table 1 shows the phase transition behavior of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). As can be seen from this table, the freshly prepared (virgin) sample of compound **4** showed a hexagonal ordered columnar (Col_{ho}) at room temperature, and cleared into isotropic liquid (I.L.) at 132.0 °C. When the I.L. was slowly cooled, it transformed into a rectangular ordered columnar ($Col_{ro}(P2_1/a)$) mesophase. When the I.L. was very rapidly cooled into rt, the Col_{ho} mesophase was obtained again.

This unique phase transition behavior can be rationally explained by using free energy *vs*. temperature (G-T) diagram. Figure 1 illustrates a G-T diagram for [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). Compound **4** gives an unstable Col_{ho} mesophase at rt for the virgin sample. When it is **rapidly** heated from rt (Step 1), it clears into I.L. at 132.0 °C with partially relaxing into another more stable mesophase of $Col_{ro}(P2_1/a)$ (Step 2a). When it is **slowly** heated from rt (Step 1), it completely relaxes into the stable mesophase of $Col_{ro}(P2_1/a)$ (Step 2b) and on further heating (Step 3), it cleared at 136.0 °C. Once it is heated over the c.p. of $Col_{ro}(P2_1/a)$ at 136.0 °C and then the resulted I.L. is **slowly** cooled (Step 4), it gives the stable $Col_{ro}(P2_1/a)$ mesophase (Step 4). On the other hand, when I.L. is very **rapidly** cooled into rt (Step 5), it gives again the unstable Col_{ho} mesophase without the relaxation into the stable $Col_{ro}(P2_1/a)$ mesopahse.

The stable $Col_{ro}(P2_1/a)$ mesophase gave a natural texture on very slow cooling from the I.L., whereas the unstable Col_{ho} mesophase could not give a natural texture because it always transformed into stable Col_{ro} mesophase on slow cooling. Figure 2 shows a well-developed natural texture of the stable $Col_{ro}(P2_1/a)$ mesopahse of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). This texture could be obtained at 79.0 °C, when the I.L. over the c.p.s was very slowly cooled at a rate of 0.1 °C/min.

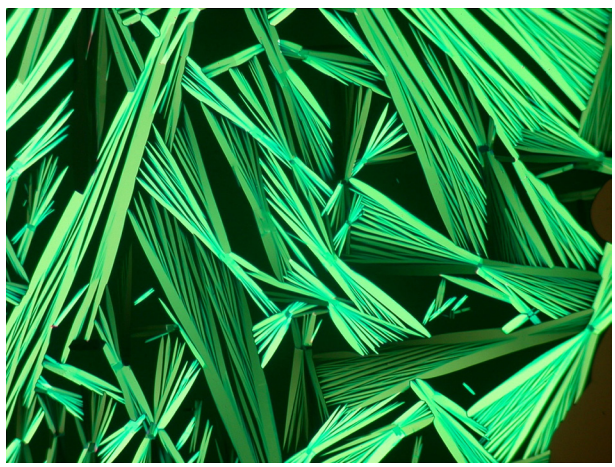


Fig. 2. Texture of the $Col_{ro}(P2_1/a)$ mesophase of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) at 79.0 °C

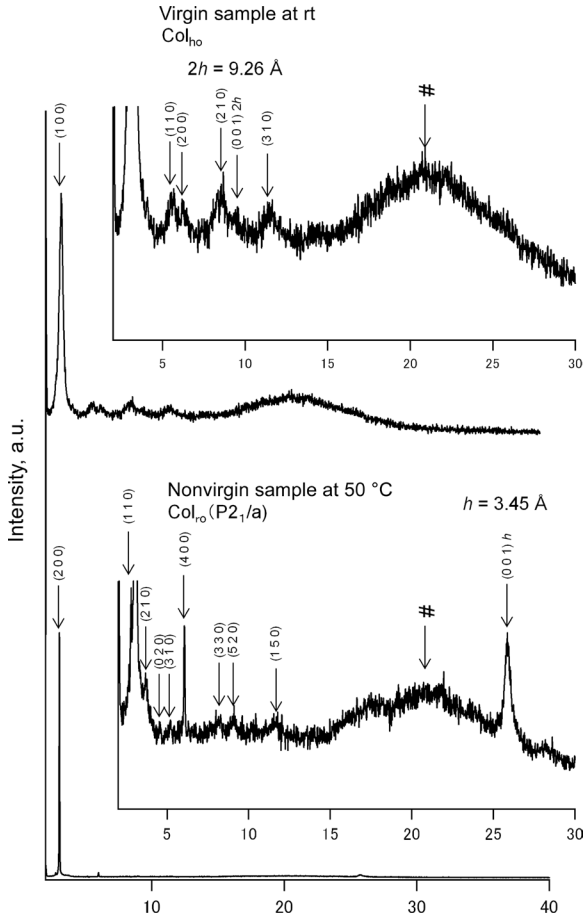


Fig. 3. XRD patterns of the virgin sample at rt and the non-virgin sample at 50 °C for [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). *h* = Stacking distance, # = Halo

This dendric texture is characteristic to a texture of Col$_r$ mesophase.

Figure 3 shows X-ray diffraction patterns of the virgin sample at rt and the non-virgin sample at 50 °C for [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**). These X-ray data are summarized in Table 2. As can be seen from this table, the virgin sample gave (100), (110), (200), (210) and (310) reflections from a 2D hexagonal lattice and (001) reflection due to an intradimer stacking distance (2h) in the low angle region. From these reflections, this mesophase could be identified as a Col$_{ho}$ mesophase. The non-virgin sample at 50 °C gave nine reflections from a rectangular lattice in the low angle region. In the high angle region, the non-virgin sample gave a very broad halo (#) due to the molten oligoether chains and a very sharp peak (0 0 1) due to a stacking distance (h) at 3.45 Å. From these reflections, this mesophase could be identified as a Col$_{ro}$ mesophase.

It is noteworthy that the present stacking distance (h = 3.45 Å) is very short for a Col$_r$ mesophase. We thought that such a short stacking distance of Col$_r$ mesophase might have originated from the very small tilt angle of molecules in the columns. We calculated the tilt angle from the slipped stacking structure illustrated in Fig. 4. As can be seen from this figure, the disk-like molecules pile up one-dimensionally with tilting to form the columns in a Col$_{ro}$ mesophase. Notations of a, b and θ in this figure represent the stacking distance, intermolecular distance and tilted angle, respectively. The tilted angle θ can be calculated from an equation: θ = arccos (b/a). The stacking distance (a) is 3.45 Å from the XRD measument. The intermolecular distance (b) can be regarded to be

Table 2. X-ray data of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**)

Mesophase	Lattice constants/Å	Spacing/Å		Miller indices (h k 1)
		Observed	Calculated	
Col$_{ho}$ at	a = 31.5	27.2	27.2	(1 0 0)
vigrin sample at r.t.	*h* = 9.26	15.8	15.7	(1 1 0)
	Z = 2.1 for ρ = 1.0	14.2	13.6	(2 0 0)
		10.3	10.3	(2 1 0)
		9.26	—	2*h*
		7.68	7.68	(3 1 0)
		ca. 4.2	—	#
Col$_{ro}$ (P2$_1$/a) at	a = 57.2 b = 37.9	31.6	31.6	(1 1 0)
nonvirgin sample at 50 ºC	*h* = 3.45	28.6	28.6	(2 0 0)
	Z = 1.8 for ρ = 1.0	23.4	22.8	(2 1 0)
		19.1	18.9	(0 2 0)
		16.9	17.0	(3 1 0)
		14.5	14.3	(4 0 0)
		10.7	10.5	(3 3 0)
		9.76	9.79	(5 2 0)
		7.54	7.56	(1 5 0)
		ca. 4.2	—	#
		3.45	—	*h*

#: Halo of the molten oligoether chains. *h*: Stacking distance.

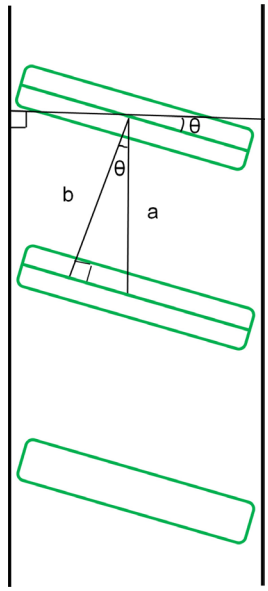


Fig. 4. Structure of stacking in the $Col_{ro}(P2_1/a)$ mesophase for [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**)

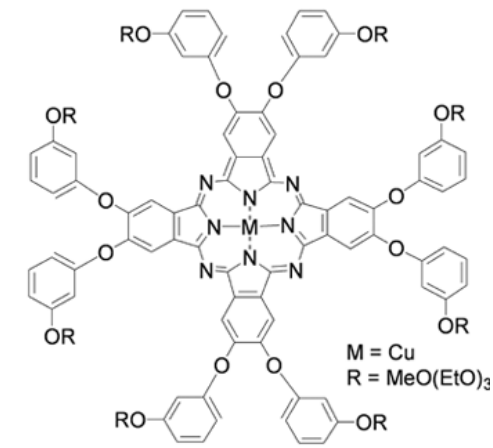
3.33 Å, which was observed as a stacking distance in the Col_{ho} mesophase for the homologous phthalocyaninato copper (II), (*m*-C_{12}OPh)$_8$PcCu (**3**), reported in our previous work [23]. This stacking distance 3.33 Å can be the intermolecular distance between phthalocyanine disks due to van der Waals forces. Therefore, θ = arccos (3.33/3.45) = 15.2°. It is very interesting that the tilted angle is very small in comparison with conventional Col_{ro} mesophases.

Solubilities

In Table 3 the solubilities of a donor (p-type) of the present [*m*-MeO(EtO)$_3$PhO]PcCu complex (**4**) and an acceptor (n-type) of the previous $(C_{10}O)_{16}$TzCu complex (**5**) [23] are summarized. These solubilities were checked for 1 mg of the sample in 1 mL of a solvent. The marks of X, Δ and O mean "insoluble," "partially soluble" and "soluble," respectively. In this table, the solvents are listed in an order of their polarities. As can be seen from this table, [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) is insoluble in

Table 3. Solubilities of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and $(C_{10}O)_{16}T_ZCu$ (**5**)

	1	5	
n-hexane	×	○	*
toluene	○	○	
Et_2O	△	○	
$CHCl_3$	○	○	
AcOEt	○	△	
THF	○	○	
CH_2Cl_2	○	○	
$(CH_3)_2CO$	○	×	*
EtOH	○	×	*
MeOH	○	×	*
H_2O	△	×	



1

5

○ soluble, △ partially soluble, × insoluble, * antagonist solubility.

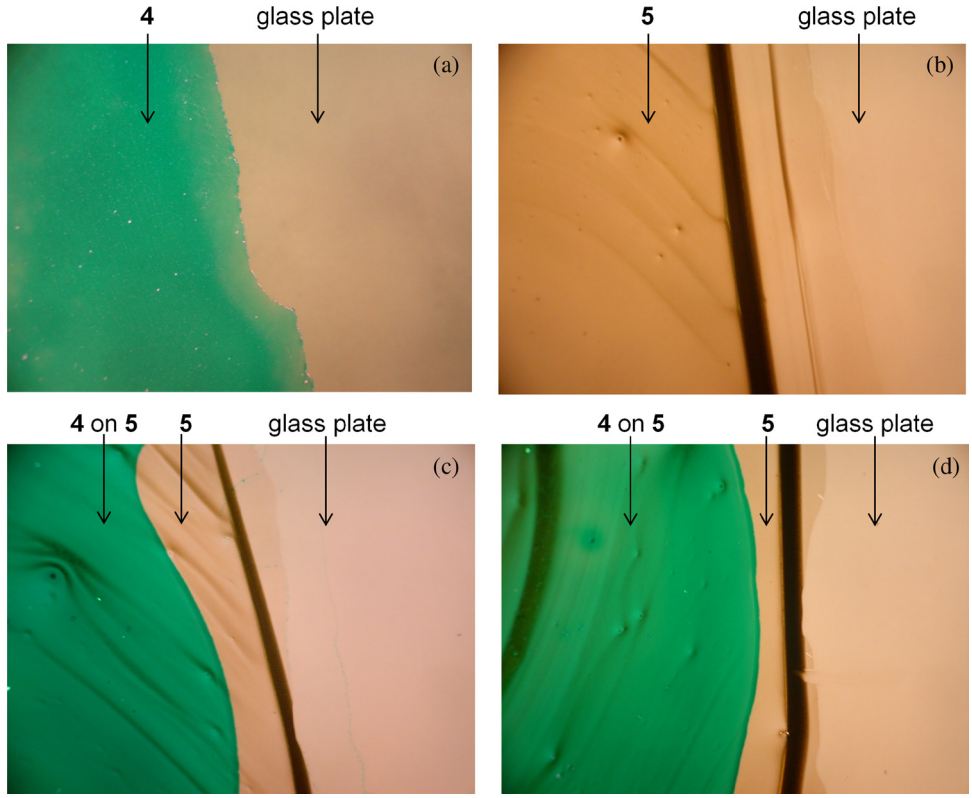


Fig. 5. Photomicrographs of the thin films of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and/or (C$_{10}$O)$_{16}$T$_Z$Cu (**5**) on a glass plate

n-hexane, whereas it is soluble in many kinds of solvents like toluene, chloroform~MeOH; and partially soluble in diethyl ether and/or water. These good solubilities in a polar solvent like acetone, ethanol and methanol are attributable to the oligoether chains in the derivatives **4**. On the contrary, (C$_{10}$O)$_{16}$TzCu (**5**) is soluble in *n*-hexane~chloroform, THF and dichloromethane, whereas it is insoluble in a polar solvent like as acetone~water. Thus antagonist solubilities could be observed between [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and (C$_{10}$O)$_{16}$TzCu (**5**). Antagonist solubility means that one compound is soluble but another compound is insoluble in the same solvent. As can be seen from Table 3, the antagonist solubilities between [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and (C$_{10}$O)$_{16}$TzCu (**5**) appear in an apolar solvent of *n*-hexane and polar solvents of acetone, ethanol and methanol.

Preparation of a double thin film by using antagonist solubility

Next we prepared a double thin film by using the antagonist solubilities of **4** and **5** in ethanol, in order to obtain the p-n junction. Figures 5a and 5b show two single thin films prepared by casting an ethanol solution of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and a chloroform solution of (C$_{10}$O)$_{16}$TzCu (**5**) onto a glass plate, respectively. Figures 5c and 5d show two double thin films prepared by casting the ethanol solution of **4** onto the thin film previously prepared by casting the chloroform solution onto a glass plate. As can be seen from Figs 5c and 5d, the compounds **4** and **5** did not mingle with each other but layered. These successful double thin films are attributable to the antagonist solubilities of **4** and **5** in ethanol (Table 3). Thus, we succeeded in preparation of a p-n junction of the doubly layered thin films by using antagonist solubility.

CONCLUSION

We successfully synthesized a novel phthalocyaninato copper (II) complex, [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) substituted by hydrophilic oligoether chains at the *m*-positions of phenoxy groups. Very interestingly, the complex **4** showed a hexagonal ordered columnar (Col$_{ho}$) mesophase for the virgin sample, whereas it showed a rectangular ordered columnar (Col$_{ro}$(P2$_1$/a)) mesophase for the non-virgin sample. Moreover, the Col$_{ho}$ mesophase gave a dimer stacking distance at 9.26 Å, whereas the Col$_{ro}$ mesophase gave a short monomer stacking distance at 3.45 Å. The complex **4** is readily soluble in polar solvents such as acetone, ethanol and methanol, which is attributable to the oligoether chains. Antagonist solubilities between p-type of [*m*-MeO(EtO)$_3$PhO]$_8$PcCu (**4**) and n-type of (C$_{10}$O)$_{16}$TzCu (**5**) enabled us to prepare a p-n junction between the doubly layered thin films of **4** and **5**. This easy preparation method of a p-n junction can be applied to organic thin film solar cell fabrications.

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REFERENCES

1. Watson MD, Fechtenkotter A and Müllen K. *J. Am. Chem. Soc*. 2006; **128**: 9526–9534.
2. Wu J, Watson MD, Zhang L, Wang Z and Müllen K. *J. Am. Chem. Soc*. 2004; **126**: 177–186.
3. Laschat S, Baro A, Steinke N, Giesselmann F, Hagele C, Scalia G, Judele R, Kapatsina E, Sauer S, Schreivogel A and Tosoni M. *Angew. Chem., Int. Ed*. 2007; **46**: 4832–4887; Kumar S. *Chem. Soc. Rev*. 2006; **35**: 83–109.
4. Ohta K, Nguyen-Tran H.-D, Tauchi L, Kanai Y, Megumi T and Takagi Y. *Handbook of Porphyrin Science*, Vol. 12, World Scientific Publishing: Singapore, 2011; pp 1–120.
5. van de Craats AM, Warman JM, Fechtenkötter A, Brand JD, Harbison MA and Müllen K. *Adv. Mater*. 1999; **11**: 1469–1472.
6. Cornil J, Lemaur V, Calbert JP and Brédas JL. *Adv. Mater*. 2002; **14**: 726–729.
7. Sergeyev S, Pisula W and Geerts YH. *Chem. Soc. Rev*. 2007; **36**: 1902–1929.
8. Nelson J. *Science* 2001; **293**: 1059–1060.
9. Schmidt-Mende L, Fechtenkötter A, Müllen K, Moons E, Friend RH and MacKenzie JD. *Science* 2001; **293**: 1119–1122.
10. Lussem G and Wendorff JH. *Polym. Adv. Technol*. 1998; **9**: 443–460.
11. Bacher A, Erdelen CH, Paulus W, Ringsdorf H, Schmidt HW and Schuhmacher P. *Macromolecules* 1999; **32**: 4551–4557.
12. Katsuhara M, Aoyagi I, Nakajima H, Mori T, Kambayashi T, Ofuji M, Takanishi Y, Ishikawa K, Takezoe H and Hosono H. *Synth. Met*. 2005; **149**: 219–223.
13. Pisula W, Menon A, Stepputat M, Lieberwirth I, Kolb U, Tracz A, Sirringhaus H, Pakula A and Müllen K. *Adv. Mater*. 2005; **17**: 684–689.
14. Boden N, Bushby RJ, Clements J and Movaghar B. *J. Mater. Chem*. 1999; **9**: 2081–2086.
15. Barberá J, Garcés AC, Jayaraman N, Omenat A, Serrano JL and Stoddart JF. *Adv. Mater*. 2001; **13**: 175–180.
16. Gearba RI, Lehmann M, Levin J, Ivanov DA, Koch MHJ, Barberá J, Debije MG, Piris J and Geerts YH. *Adv. Mater.* 2003; **15**: 1614–1618.
17. van de Craats AM, Warman JM, Hasebe H, Naito R and Ohta K. *J. Phys. Chem. B* 1997; **101**: 9224–9232.
18. Sullivan P, Heutz S, Schultes SM and Jones TS. *Appl. Phys. Lett*. 2004; **84**: 1210–1212.
19. McHale G, Newton MI, Hooper PD and Willis MR. *Optical Materials* 1996; **6**: 89–92.
20. Thiebaut O, Bock H and Grelet E. *J. Am. Chem. Soc.* 2010; **132**: 6886–6887.
21. Ban K, Nishizawa K, Ohta K, van de Craats AM, Warman JM, Yamamoto I and Shirai H. *J. Mater. Chem*. 2001; **11**: 321–331.
22. Ichihara M, Suzuki A, Hatsusaka K and Ohta K. *J. Porphyrins Phthalocyanines* 2007; **11**: 503–512.
23. Ichihara M, Miida M, Mohr B and Ohta K. *J. Porphyrins Phthalocyanines* 2006; **10**: 1145–1155.
24. Peterca M, Percec V, Imam MR, Leowanawat P, Morimitsu K and Heiney PA. *J. Am. Chem. Soc.* 2008; **130**: 14840–14852.
25. Xu H, Jiang XJ, Chan EYM, Fong WP and Ng DKP. *Org. Biomol. Chem.* 2007; **5**: 3987–3992.
26. Hasebe H, Master Thesis, Shinshu University, Ueda, 1991; Ema H, Master Thesis, Shinshu University, Ueda, 1988.

