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Discotic Liquid Crystals of Transition Metal Complexes, 19:* Discotic Mesomorphism and Double Clearing Behavior of Octakis(dialkoxyphenyl)phthalocyanine Derivatives

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Eight novel octakis(3,4-dialkoxyphenyl)-phthalocyanine derivatives, Cn-M (2, M=2H; 3, M=Ni; 4, M=Cu; a, decyloxy; b, undecyloxy; c, dodecyloxy), have been synthesized and characterized. It was found that each of the derivatives exhibits discotic liquid crystalline properties, and that each of the Cn–Cu (4) derivatives has two kinds of $D_{rd2}(P2_1/a)$ mesophases. These Cn–Cu (4a,b,c) and C_{12}–2H (2c) derivatives exhibit a unique double clearing behavior.

Keywords: phtholocyonines; double clearing behavior; discotic liquid crystal; mesophase

1 INTRODUCTION

Phthalocyanine (Pc) is well known as a disk-like molecule and forms a one-dimensional columnar structure in condensed phases. In 1982, Simon and co-workers synthesized a peripherally octa-alkoxymethyl-substituted Pc derivative which exhibits a discotic hexagonal columnar (Dh) mesophase.[2] Since then, a great variety of liquid-crystalline Pc derivatives have been synthesized and show a Dh mesophase in most cases.[2,3] A few Pc derivatives exhibit other mesophases. A crown-ether-substituted Pc shows a peculiar mesophase with a square lattice.[4] A chiral-chain-substituted Pc shows a discotic cholesteric (N^*_D) mesophase.[5] A 2-ethylhexyloxy-substituted Pc exhibits both a discotic tetragonal disordered columnar (Dtet.d) phase and a discotic nematic (N_D) phase.[6] A polymeric Pc and a strip-like dimeric Pc derivative exhibits a lamellar phase.[7] Thus, various mesophases appear corresponding to the peripheral substituent groups introduced into the Pc core. These peripheral substituents are, however, neither bulky nor rigid. Peripheral groups offering steric hindrance may prevent the Pc molecules from stacking one-dimensionally and exert a great influence on the mesomorphic properties, e.g. a decrease in clearing and melting points. Furthermore, Pc compounds substituted with such steric-hindrance groups can become readily soluble in many organic solvents,[8] although Pc compounds are believed to be insoluble in organic solvents. Hence, we previously prepared octakis(alkoxyphenyl)-substituted Pc derivatives (**1**).[9] The phenyl groups provide rigid steric hindrance around the Pc core because the two neighboring phenyl groups cannot rotate freely. These metal-free and copper(II) derivatives (**1**) exhibit a Dhd phase and a discotic rectangular disordered columnar (Drd) phase, respectively. They are also easily soluble in various organic solvents (e.g. dichloromethane, chloroform, benzene and carbon tetrachloride). However, compounds **1** decompose in two steps on heating: the first decomposition is most likely to be caused by a ring-closure at the *ortho*-position of the two neighboring phenyl groups. Hence, in this work we have prepared eight novel octakis(dialkoxyphenyl)-substitute Pc derivatives **2**, **3** and **4**, because the additional alkoxy group at the *meta*-position of the phenyl groups may effectively prevent the ring-closure reaction between the adjacent two phenyl groups on heating. We wish to report here that these novel Pc derivatives (**2**, **3**, **4**) do not decompose by the ring-closure reaction on heating, and that each of the

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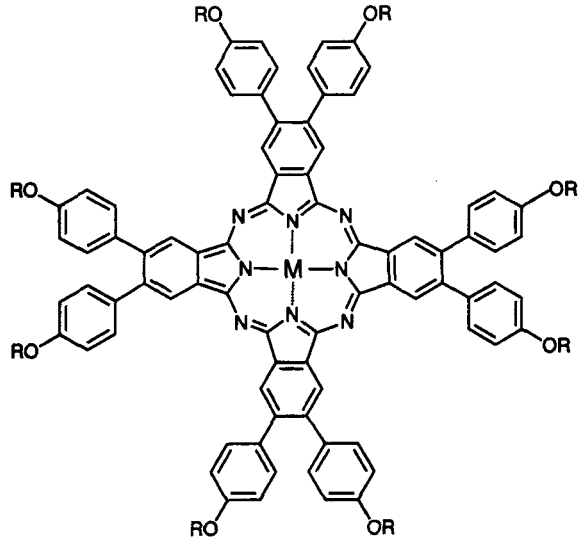
compounds **4** has two kinds of Drd($P2_1/a$) mesophases and exhibits a unique 'double clearing' behavior between two discophases which has not been reported to date.

2 EXPERIMENTAL

2.1 Synthesis

The synthetic route to the octakis(3,4-dialkoxyphenyl)phthalocyanines **2** (abbreviated as Cn–2H, $n=10$, 11, 12) and the corresponding metal(II) complexes **3**, **4** (Cn–Ni and Cn–Cu) is shown in Scheme 1. The precursors **5** were prepared by the method previously reported for $n=10$ (**a**).[9] Dicyanoacetylene **7** was also obtained in two steps according to the previously described procedure.[9] The final Pc derivatives, **2–4**, were synthesized through **6** in a similar manner to the octakis(4-alkoxyphenyl)phthalocyanine derivatives.[9] The yields and elemental analysis data of the final products are listed in Table 1, and the electronic spectral data are summarized together with the related compounds



1

M = 2H R = C_nH_{2n+1} n = 8, 10, 12, 18

M = Cu R = C_nH_{2n+1} n = 10, 12, 18

Structure 1.

in Table 2. The detailed procedures are described below only for the compounds substituted with dodecyloxy groups (**c**), because the other compounds, bearing decyloxy (**a**) and undecyloxy (**b**) groups, could be synthesized in the same manner.

2.1.1 3,3′,4,4′-Tetra-n-undecyloxybenzil (5b)

Yield 74%, m.p. 97 °C.

2.1.2 3,3′,4,4′-Tetra-n-dodecyloxybenzil (5c)

Yield 79%, m.p. 95 °C.

2.1.3 3,4-Bis(3,4-didodecyloxyphenyl)-4-hydroxy-2-cyclopenten-1-one (6c)

A mixture of 1.42 g (1.55 mmol) of 3,3′,4,4′-tetra-n-dodecyloxybenzil (**5c**), 0.90 g (0.80 mmol) of potassium *t*-butanolate, and 1.80 g (31 mmol) of acetone in a mixture of 60 ml of dry ethanol and 20 ml of dry tetrahydrofuran was refluxed under nitrogen for 17 h. After cooling to room temperature, the reaction mixture was poured into 100 ml of a 2% aqueous acetic acid solution and extracted with chloroform. The organic layer was washed with water, dried over sodium sulfate and evaporated to dryness. The purification was performed by column chromatography over silica gel with a mixture of chloroform and ethyl acetate (5:1, v/v; $R_f=0.60$) and then by recrystallization from ethanol to give 1.10 g of white powder, yield 68%.

^{1}H-NMR ($CDCl_3$, TMS): $\delta=6.93$–6.67 (m, 6H, Ph), 6.47 (s, 2H, olefin) 3.93 (t, 8H, OCH_2), 2.86 (s, 2H, CH_2CO), 2.47 (s, 1H, OH), 1.25 (m, 80H, CH_2), 0.88 (t, 12H, CH_3).
IR (KBr, cm^{-1}): 3320 (OH), 2900, 2850 (CH_2), 1660 (CO), 1580, 1500 (Ph), 1250 (OPh).
Elemental analysis, $C_{65}H_{110}O_6$ (M_w 987.60): Calcd(%): C, 79.05; H 11.23; Found: C, 78.71; H, 10.97%.

This compound exhibits mesomorphism. Its phase transition behavior (Scheme 2) was established by microscopical observations, DSC measurements and X-ray diffraction. The mesophase was confirmed as a smectic A (S_A) phase.

2.1.4. 3.4-Bis(3,4-didecyloxyphenyl)-4-hydroxy-2-cyclopenten-1-one (6a)

The purification was twice carried out by column chromatography over silica gel with a mixture of chloroform and ethyl acetate (15:1, v/v, $R_f=0.60$) to give a yellow syrup of **6a** in 60%

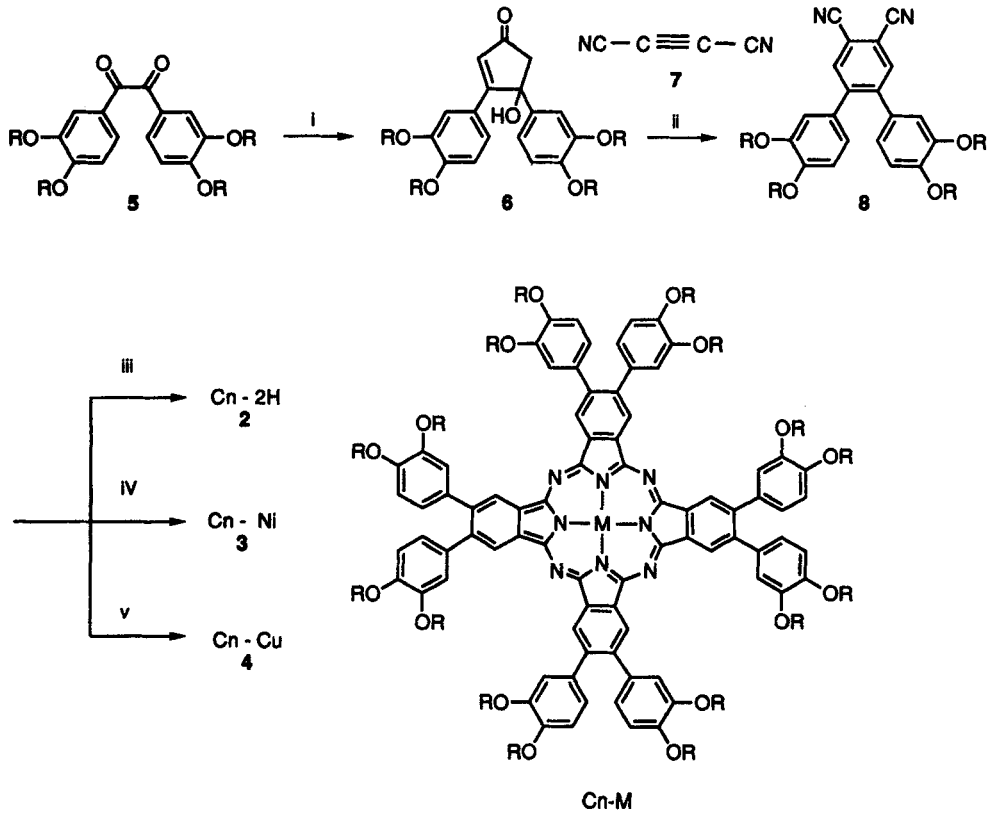
yield with clearing point S_A 51.1 °C I.L. (isotropic iquid).

2.1.5 3,4-Bis(3,4-diundecyloxyphenyl)-4-hydroxy-2-cyclopenten-1-one (6b)

The purification is the same as that of **6a**, i.e. using $CHCl_3/CH_3CO_2Et = 15:1$, v/v, $R_f = 0.60$ to give a yellow syrup, yield 54% and clearing point S_A 51.5 °C I.L.

2.1.6 3,3′,4,4′-Tetradodecyloxy-*o*-terphenyl-4′,5′-dicarbonitrile (8c)

An excess of dicyanoacetylene (**7**) and 0.65 g (0.66 mmol) of the cyclopentenone derivative (**6c**) in 20 ml of chlorobenzene in a special flask[10]



	R = C_nH_{2n+1}		
	a	**b**	**c**
	n=10	n=11	n=12
2: M = 2H	C_{10}-2H	C_{11}-2H	C_{12}-2H
3: M = Ni	C_{10}-Ni	C_{11}-Ni	
4: M = Cu	C_{10}-Cu	C_{11}-Cu	C_{12}-Cu

Scheme 1. Reagents: i, 0.52 eq. potassium t-butanolate, 20 eq. acetone, ethanol reflux, 17 h; ii, excess dicyanoacetylene (**7**), 0.01 eq. *p*-toluenesulfonic acid, chlorobenzene, 60–70 °C, 1 h; reflux, 20 min; iii, 1.5 eq. DBU, n-pentanol, reflux, 17 h; iv, v, 2 eq. $NiBr_2$ or $CuCl_2$, 1.5 eq DBU, n-pentanol, reflux, 17 h (eq=equivalent).

Table 1 Yields and elemental analysis data of the Cn–Cu derivatives

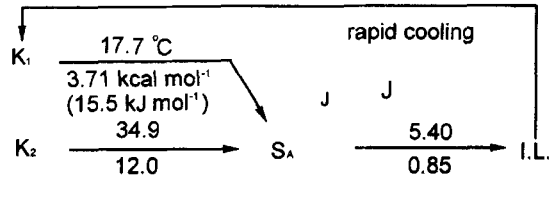
Compound		Yield (%)	Mol. formula (Mol. wt)	Elemental analysis: Found (Calcd) (%) N	C	H
2a	C_{10}–2H	3	$C_{240}H_{370}N_8O_{16}$ (3623.66)	2.85 (3.09)	80.09 (79.55)	10.57 (10.29)
2b	C_{11}–2H	55	$C_{256}H_{402}N_8O_{16}$ (3848.05)	2.85 (2.91)	80.29 (79.91)	10.57 (10.53)
2c	C_{12}–2H	31	$C_{282}H_{434}N_8O_{16}$ (4072.48)	2.84 (2.75)	80.26 (80.22)	11.11 (10.74)
3a	C_{10}–Ni	7	$C_{240}H_{368}N_8O_{16}Ni$ (3680.34)	2.86 (3.05)	78.68 (78.33)	10.31 (10.08)
3b	C_{11}–Ni	13	$C_{256}H_{400}N_8O_{16}Ni$ (3904.97)	2.48 (2.87)	76.35 (78.74)	10.24 (10.33)
4a	C_{10}–Cu	38	$C_{240}H_{368}N_8O_{16}Cu$ (3685.15)	3.05 (3.04)	78.07 (78.22)	10.05 (10.07)
4b	C_{11}–Cu	60	$C_{256}H_{400}N_8O_{16}Cu$ (3909.62)	2.85 (2.87)	78.72 (78.65)	10.31 (10.31)
4c	C_{12}–Cu	66	$C_{282}H_{432}N_8O_{16}Cu$ (4134.01)	2.81 (2.71)	78.83 (79.03)	10.42 (10.53)

were stirred under nitrogen and maintained at 60–70 °C. A solution of 1.3 mg (6.6 μmol) of *p*-toluenesulfonic acid in 0.1 ml of 1,4-dioxane was added dropwise. The mixture was stirred for 1 h and then heated under reflux for 20 min to complete the reaction. The solvent was evaporated to dryness and the residue was dried *in vacuo*. After chromatography (SiO_2, $CHCl_3$) the pure product was obtained (R_f=0.74) as pale yellow plate-like crystals, yield 0.63 g (94%), m.p.=40 °C.

^{1}H-NMR ($CDCl_3$, TMS): δ=7.70 (s, 2H, Ph) 6.70–6.47 (m, 65H, Ph), 3.90 (t, 4H, CH_2), 3.63 (t, 4H, CH_2), 1.30 (m, 80H, CH_2), 0.86 (t, 12H, CH_3).
IR (KBr, cm^{-1}): 2910, 2860 (CH_2), 2220 (CN), 1590, 1510 (Ph), 1250 OPh).

2.1.7 3,3″,4,4″-Tetradecyloxy-*o*-terphenyl-4′,5′-dicarbonitrile (8a)

The purification was carried out only by chromatography (SiO_2 gel, benzene, R_f=0.66) to give a yellow syrup of **8a** in 91% yield. This material is not liquid-crystalline.



Scheme 2. Phase transition behavior of compound **6c**.

2.1.8 3,3″,4,4″-Tetraundecyloxy-*o*-terphenyl-4′,5′-dicarbonitrile (8b)

The purification was the same as that of **8a** (SiO_2 gel, benzene, R_f=0.66). A yellow syrup, yield 86%, was produced.

2,3,9,10,16,17,23,24-Octakis(3,4-didodecyloxyphenyl)phthalocyanine (2c)

A mixture of 0.60 g (0.59 mmol) of the dicarbonitile derivative (**8c**) and 0.13 g (0.88 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 10 ml of n-pentanol was refluxed under a nitrogen atmosphere for 17 h. After the reaction mixture had been cooled to room temperature, ethanol was added to it and the resulting precipitate was collected by filtration, washed with ethanol and then dried. The crude product was purified by column chromatography over silica gel with benzene (R_f=0.98) and then by recrystallization from ethyl acetate to give 0.19 g of dark green powder in 31% yield.

^{1}H-NMR ($CDCl_3$, TMS): δ=9.28 (bs, 8H, Pc benzo ring), 7.26–6.90 (m, 24H, Ph), 4.06 (t, 16H. OCH_2), 3.57 (t, 16H, OCH_2), 1.91 (quintet, 16H, CH_2), 1.71 (quintet, 16H, CH_2), 1.57–1.20 (m, 288H, CH_2), 0.91 (t, 24H, CH_3), 0.84 (t, 24H, CH_3), −1.26 (bs, 1H, NH), −1.34 (bs, 1H, NH).

Table 2 UV–Vis is spectral data of Cn–M and the related Pc derivatives

Compound	Concentration[a] (mol l^{-1})	λ_{max} (nm) (log ε)						
					Q_{y0-1}	Q_{x0-1}	Q_{y0-0}	Q_{x0-0}
2a C_{10}–2H	1.01×10^{-5}	308.9 (4.88)	345.3 (4.88)	ca. 440 (4.48 sh)	626.5 (4.52)	659.8 (4.66)	691.5 (5.16)	725.0 (5.23)
2b C_{11}–2H	1.19×10^{-5}	308.9 (4.93)	344.4 (4.93)	ca. 440 (4.50 sh)	626.4 (4.57)	660.5 (4.71)	691.5 (5.23)	724.9 (5.30)
2c C_{12}–2H	1.02×10^{-5}	296.2 (4.98)	345.0 (4.95)	ca. 440 (4.52 sh)	626.7 (4.60)	660.4 (4.74)	691.8 (5.27)	725.0 (5.34)
					Q_{0-1}	Aggregate	Q_{0-0}	
3a C_{11}–Ni	$1.07\times10^{-}$	314.5 (5.09)	ca.330 (sh)	421.4 (4.46)	624.7 (4.65)	668.0 (4.70)	694.7 (5.41)	
3b C_{11}–Ni	1.06×10^{-5}	314.5 (5.07)	ca. 330 (sh)	417.9 (4.48)	625.0 (4.63)	668.0 (4.68)	695.4 (5.40)	
4a C_{10}–Cu	1.01×10^{-5}	305.9 (4.31)	341.4 (4.39)	420.4 (4.48)	631.8 (3.48)	673.3 (3.73)	703.7 (5.47)	
4b C_{11}–Cu	0.937×10^{-5}	305.4 (4.95)	342.5 (4.98)	420.9 (4.47)	632.0 (4.75)	673.8 (4.70)	704.0 (5.51)	
4c C_{12}–Cu	0.710×10^{-5}	305.5 (4.95)	342.0 (4.99)	421.5 (4.49)	631.9 (4.76)	673.8 (4.72)	704.3 (5.53)	
Ph_8PcCu[b]	In chloroform		356 [1][c]	380 [0.43 sh]	628 [0.45]	665 [0.38]	698 [2.28]	
PcCu[d]	In chlorobenzene				611 (4.56)	648 (4.51)	678 (5.34)	
$(C_8O)_8PcCu$[c]	In chloroform				610 (4.75)	644-52 (sh)	675 (5.65)	

[a] In $CHCl_3$, unless otherwise indicated.
[b] Ref. 14.
[c] Relative intensity.
[d] Ref. 12.
[e] Ref. 13.

IR (KBr, cm^{-1}): 2950, 2920, 2850, 1600, 1520, 1270, 1250.

2.1.10 2,3,9,10,16,17,23,24-Octakis(3,4-didecyloxyphenyl)phthalocyanine (2a)

The crude product was purified by column chromatogrpahy over silica gel with benzene (R_f=1.00). Then precipitation was carried out in methanol with an ethyl acetate solution to give a dark green syrup in 3% yield.

2.1.11 2,3,9,10,16,17,23,24-Octakis(3,4-diundecyloxyphenyl)phthalocyanine (2b)

The purification was the same as that of **2c**. A ductile dark green solid, yield 55%, was produced.

Table 3 Phase transition temperatures (T) of CnO–Cu (**2**, **3**, **4**)

Compound		Phase $\overset{T(°C)}{\rightarrow}$ Phase[a]	
2a	C_{10}–2H	X $\overset{56}{\rightleftharpoons}$ D_1 $\overset{106}{\rightleftharpoons}$ D_2 $\overset{184}{\rightleftharpoons}$ I.L.	b
2b	C_{11}–2H	X $\overset{66}{\rightleftharpoons}$ D $\overset{190}{\rightleftharpoons}$ I.L.	b
2c	C_{12}–2H	D $\overset{66}{\rightleftharpoons}$ D_{rd1} $\overset{185.6}{\rightleftharpoons}$ D_x[c] $\overset{187.2}{\rightleftharpoons}$ I.L.; D_{rd1} $\overset{185.9}{\rightarrow}$ I.L. (slow)	
3a	C_{10}–Ni	X $\overset{59}{\rightleftharpoons}$ D_1 $\overset{100}{\rightleftharpoons}$ D_2 $\overset{175}{\rightleftharpoons}$ I.L.	b
3b	C_{11}–Ni	X $\overset{58}{\rightleftharpoons}$ D $\overset{195}{\rightleftharpoons}$ I.L.	b
4a	C_{10}–Cu	D $\overset{75}{\rightleftharpoons}$ D_{rd1} $\overset{196}{\rightleftharpoons}$ D_{rd2} $\overset{219}{\rightleftharpoons}$ I.L.; D_{rd1} $\overset{217}{\rightarrow}$ I.L. (slow)	
4b	C_{11}–Cu	D $\overset{72}{\rightleftharpoons}$ D_{rd1} $\overset{185}{\rightleftharpoons}$ D_{rd2} $\overset{204}{\rightleftharpoons}$ I.L.; D_{rd1} $\overset{199}{\rightarrow}$ I.L. (slow)	
4c	C_{12}–Cu	D $\overset{72}{\rightleftharpoons}$ D_{rd1} $\overset{192.0}{\rightleftharpoons}$ D_{rd2} $\overset{197.0}{\rightleftharpoons}$ I.L.; D_{rd1} $\overset{196.6}{\rightarrow}$ I.L. (slow)	

[a] Phase nomenclature: X, unidentified phase which was difficult to distinguish as a crystal or mesophase; D, unidentified discophase; D_{rd}, discotic rectangular disordered columnar mesophase; I.L., isotropic liquid.

[b] This sample was too small for the temperature-dependent X-ray technique to be employed. The phase sequence was determined by DSC and microscopical observations.

[c] See the main text.

~~~► indicates relaxaton.
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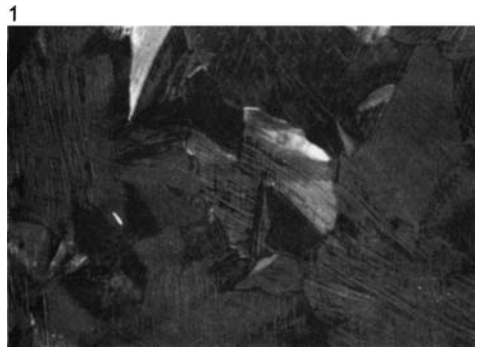
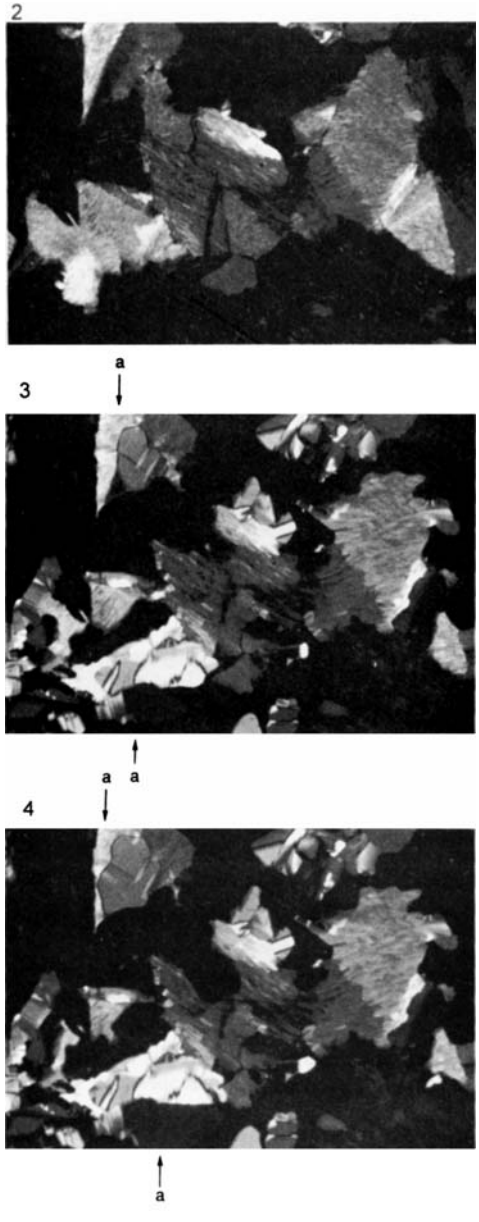
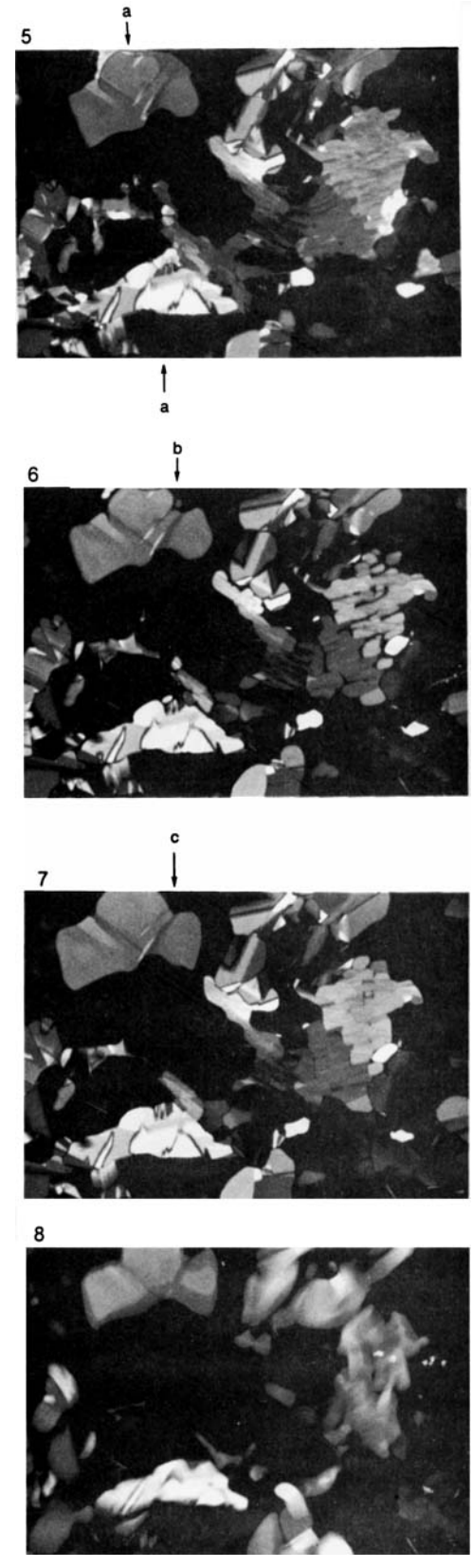


Figure 1 Photomicrographs of the 'double clearing' behavior between two discophases of C_{12}–Cu (**4c**). The changes which occur with the phase transition and relaxation are marked with arrows (a–c). For descriptions, see the main text.





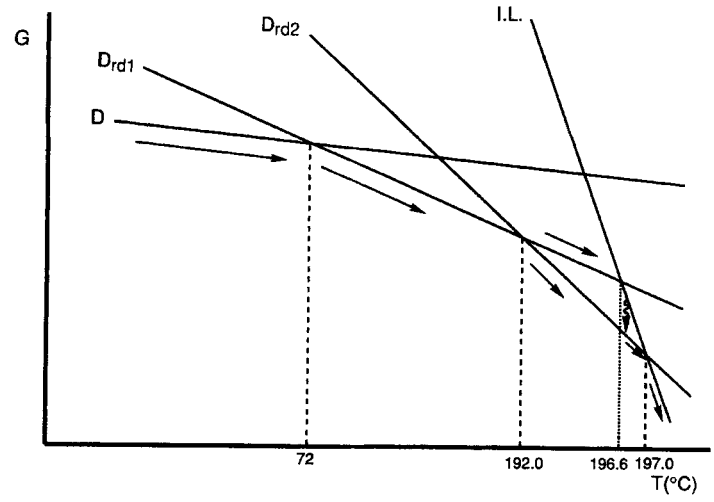


Figure 2 Schematic free energy versus temperature (G–T) diagram for C_{12}–Cu (**4c**).

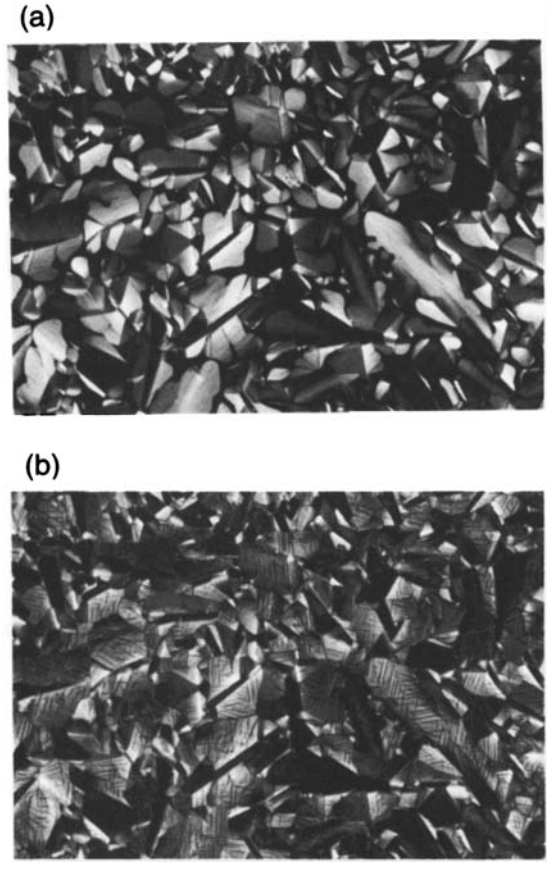


Figure 3 Natural textures of the C_{12}–2H derivatives (**2c**): (a) the D_x mesophase at 186 °C; (b) the D_{rd1} mesophase at 150 °C.

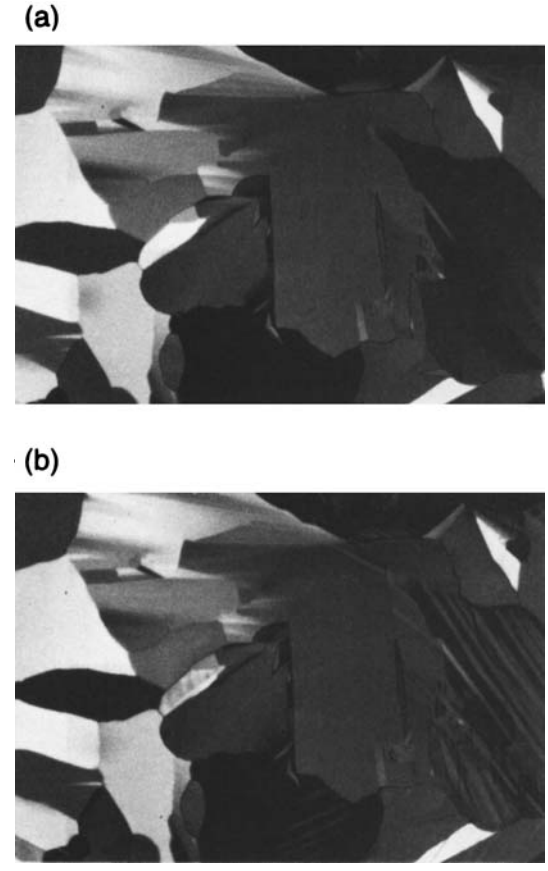


Figure 4 Natural textures of C_{12}–Cu (**4c**): (a) the D_{rd2} mesophase at 195 °C; (b) the D_{rd1} mesophase at 150 °C.

2.1.12 2,3,9,10,16,17,23,24-Octakis(3,4-didodecyloxyphenyl)phthalocyaninato copper (II) (4c)

A mixture of 0.58 g (0.57 mmol) of the dicarbonitrile derivative (**8c**), 0.13 g (0.88 mmol) of DBU, and 0.022 g (1.16 mmol) of copper(II) chloride in 10 ml of n-pentanol was refluxed under a nitrogen atmosphere for 17 h. After the reaction mixture had been cooled to room temperature, ethanol was added to it and the

Table 4 X-ray powder diffraction data of Cn–Cu (**4a**, **4b**, **4c**)

Complex	Mesophase and measured temperature	Spacing (Å)		Miller indices
		$d_{obs.}$	$d_{calcd.}$	(*h k l*)
4a C_{10}–Cu	D_{rd1} at 100 °C	32.0	32.0	(1 1 0)
		28.3	28.3	(2 0 0)
	$D_{rd}(P2_1/a)$	18.6	18.4	(1 2 0)
	a=56.6 Å	12.6	12.6	(1 3 0)
	b=38.8 Å	11.2	11.2	(4 2 0)
	D_{rd2} at 212 °C	31.1	31.9	(1 1 0)
		27.2	27.0	(2 0 0)
	$D_{rd}(P2_1/a)$	19.8	19.8	(0 2 0)
	a=54.0 Å	11.8	11.8	(2 3 0)
	b=39.5 Å			
4b C_{11}–Cu	D_{rd1} at 100 °C	36.0	36.0	(1 1 0)
		31.5	31.5	(2 0 0)
	$D_{rd}(P2_1/a)$	19.7	19.0	(3 1 0)
	a=63.1 Å	17.8	18.0	(2 2 0)
	b=43.8 Å	13.1	13.2	(2 3 0)
		9.65	9.71	(3 4 0)
		8.58	8.53	(6 3 0)
	D_{rd2} at 201 °C	33.4	35.3	(1 1 0)
		29.1	29.6	(2 0 0)
	$D_{rd}(P2_1/a)$	24.5	24.5	(2 1 0)
	a=59.1 Å	22.0	22.0	(0 2 0)
	b=43.9 Å	18.5	18.0	(3 1 0)
		15.0	14.8	(4 0 0)
		12.8	13.1	(2 3 0)
4c C_{12}–Cu	D_{rd1} at 100 °C	34.7	34.7	(1 1 0)
		30.5	30.5	(2 2 0)
	$D_{rd}(P2_1/a)$	17.7	17.4	(2 2 0)
	a=61.0 Å	15.8	15.3	(4 0 0)
	b=42.2 Å	13.6	13.7	(1 3 0)
		12.1	12.2	(5 0 0)
		9.94	9.97	(2 4 0)
		8.83	8.68	(4 4 0)
		7.95	7.98	(5 4 0)
	D_{rd2} at 196 °C	34.8	34.8	(1 1 0)
		30.1	30.1	(2 0 0)
	$D_{rd}(P2_1/a)$	24.7	24.6	(2 1 0)
	a=60.2 Å	21.9	21.3	(0 2 0)
	b=42.6 Å	18.6	18.2	(3 1 0)
		14.9	15.1	(4 0 0)
		13.0	12.9	(2 3 0)
		11.5	11.6	(3 3 0)

resulting precipitate was collected by filtration, washed with ethanol and ethyl acetate, and then dried. The crude product was purified by column chromatography over silica gel with benzene (R_f=1.0) and then by recrystallization from ethyl acetate to give 0.19 g of a dark green soft powder, yield 0.39 g (66%).

2.1.13 Other complexes

The other metal complexes(**3a**, **3b**, **4a** and **4b**) could be prepared in the same manner as **4c**.

2.2 Measurements

The products were identified by elemental analysis using a Perkin–Elmer Elemental Analyzer 240B, UV–Vis spectra using a Hitachi 330 spectrophotometer, and ^{1}H-NMR (250 MHz) spectra using a Brücker AC-250. The phase transition behavior of these compounds was observed with a heating plate controlled by a thermoregulator, Mettler FP80 and 82. To establish the mesophases, X-ray diffraction powder patterns were measured with Cu-Kα radiation using a Rigaku Geigerflex equipped with a handmade heating plate controlled by thermoregulator.[11]

3 RESULTS AND DISCUSSION

3.1 Electronic absorption spectra

In Table 2 are listed the electronic absorption spectra data of Cn–M (**2**, **3**, **4**) and the related PcCu derivatives. Cn–2H (**2**) and Cn–M (M=Ni and Cu: **3**, **4**) exhibit the typical electronic absorption spectra of metal-free Pc compounds with *D2h* symmetry and metal(II) Pc complexes with *D4h* symmetry, respectively. As can be seen from Table 2, the Q_{0-0} bands of the $(C_8O)_8$PcCu complex,[12] which is composed of the PcCu core and eight n-octyl side groups, undergoes little shift (678–675 nm). Therefore, both PcCu[13] and $(C_8O)_8$PcCu show a blue color. On the other hand, the Q_{0-0} band of the Ph_8PcCu complex,[14] which is composed of the same PcCu core and eight phenyl side groups, red-shifts 20 nm compared with that of PcCu (678–698 nm). Hence, Ph_8PcCu shows a green color. When the PcCu core is substituted by eight 3,4-dialkoxyphenyl groups, the Q_{0-0} band red-shifts about 26 nm (678–704 nm). The present Cn–Cu complexes also become green. All the other Cn–M (M=2H, Ni) derivatives also show a green color. Since all of the present Pc derivatives are readily soluble in many organic solvents at room temperature, they have great potential for application as light-fast green dyes.[15]

Furthermore, an additional peak located at 380 nm for Ph_8PcCu, at around 420 nm for the Cn–M (M=Cu, Ni) complexes, and at *ca* 440 nm for Cn–2H could be obtained. This peak can be characteristically observed for a number of phenyl-substituted phthalocyanines[16] and porphyrins.[17]

3.2 Phase transition behavior of Cn–M (2, 3, 4)

In Table 3 is summarized the phase transition behavior of the Cn–M derivatives **2**, **3** and **4**. It was established by differential scanning calorimetry and microscopical observations. The samples of **2a**, **2b**, **3a** and **3b** were too small for the temperature-dependent X-ray diffraction technique to be employed. On the other hand, the phase transition behavior of the other derivatives (**2c**, **4a**, **4b** and **4c**) could be further identified by X-ray structural analysis. Hence, the D mesophases in this Table mean the discophases which have not been further characterized by the X-ray technique. Nevertheless, each of the present Cn–M derivatives (**2**, **3**, **4**) is mesogenic and shows an isotropic liquid (I.L.) without decomposition whereas the previous eight alkoxy substituted Pc homologs (**1**) decompose on heating.[9] Hence, it is apparent that the additional alkoxy groups at the *meta*-position of the phenyl groups effectively prevent the decomposition.

3.3 'Double clearing' behavior of 4a, 4b, 4c and 2c

The Cn–Cu derivatives **4a**, **4b**, **4c** and **2c** exhibit a unique 'double clearing' behavior. A sequence of the changes of state of C_{12}–Cu (**4c**) is shown by photomicrographs in Fig. 1.

(1) The D mesophase of C_{12}–Cu (**4c**) was obtained when a D_{rd1} mesophase at 190.0 °C had been rapidly cooled to room temperature.
(2) When the sample in (1) was heated again to 190.0 °C, the D mesophase transformed into the D_{rd1} mesophase. The dark areas here show that the polarized light was shut off due to the molecular orientation: hence, they

do not correspond to the isotropic liquid.

(3) When the sample in (2) was heated to 192.0 °C from 190 °C at a rate of 1 °C min^{-1} and was then held at 192.0 °C for 10 min, a D_{rd2} mesophase formed in the D_{rd1} mesophase (see the parts marked with arrows (a)].

(4) When the sample in (2) was held at 192.0 °C for 20 min, the D_{rd2} mesophase (a) grew further in the D_{rd1} mesophase, compared with the parts marked (a) in (3).

(5) When the sample in (4) was heated to 196.4 °C from 192.0 °C at a rate of 1 °C min^{-1}, the D_{rd2} mesophase grew still further (a).

(6) When the sample in (5) was heated to 196.6 °C from 196.4 °C, the D_{rd1} mesophase was transformed into an isotropic liquid (I.L.) (b): the first clearing at 196.6 °C was apparently caused by superheating of the D_{rd1}–D_{rd2} phase transition from 192.0 °C to 196.6 °C.

(7) When the sample in (6) was held at 196.6 °C for 10 min, the I.L. was transformed into the D_{rd2} mesophase owing to relaxation from the I.L. to the D_{rd2} mesophase, and then the D_{rd2} mesophase grew (c).

(8) When the sample in (7) was heated to 197.0 °C, the D_{rd2} mesophase cleared into the I.L.: i.e. it underwent the second clearing.

Thus, a 'double clearing' behavior of C_{12}–Cu (**4c**) could be observed by using a polarizing microscope. The other derivatives **4a**, **4b** and **2c** also exhibit the same behavior as C_{12}–Cu (**4c**).

These compounds might contain a number of geometrical isomers. However, if the compounds were a mixture of the geometrical isomers with different clearing points, a relaxation phenomenon from the I.L. phase to the D_{rd2} mesophase such as that observed in Fig. 1, micrograph 7, could not occur.[18] Therefore, the compounds are geometrically pure materials.

To date, it has been reported that a 'double clearing' behavior and a 'double melting' behavior are caused by superheating of the crystal–mesophase transition[19] and the crystal–crystal phase transition,[20] respectively. However, there have been no reports until now of double clearing behavior caused by a superheating of the mesophase–mesophase tansition. The present double clearing behavior is apparently caused, not by a superheating of the crystal–crystal phase transition, but by a superheating of the mesophase (D_{rd1})–mesophase (D_{rd2}) transition (Fig. 1, micrograph 6). The superheating may originate from a small difference of the entropies between the D_{rd1} mesophase and the D_{rd2} (or D_x) mesophase. As will be described below in detail, X-ray structural analyses revealed that both D_{rd1} and D_{rd2} have the same symmetry, which means that the structural difference is small.

This double clearing behavior can be rationally explained by using a schematic Gibbs free energy versus temperatures (G–T) diagram (Fig. 2). When the C_{12}–Cu derivative (**4c**) is heated from room temperature, the D phase changes into the D_{rd1} phase at the intersection (72 °C) of the D phase line and the D_{rd1} phase line. On further heating, the D_{rd1} phase begins to transform into the D_{rd2} phase at the intersection (192.0 °C) of the D_{rd1} phase line and the D_{rd2} phase line. Since this phase transition is very slow, a part of the D_{rd1} phase is superheated without change along the D_{rd1} phase line until 196.6 °C at the intersection of the D_{rd1} phase line and the I.L. line, which is the clearing point of the D_{rd1} phase. The resulting I.L. phase at 196.6 °C is gradually relaxed into the more stable D_{rd2} phase because the free energy of the I.L. phase is higher than that of the D_{rd2} phase. On further heating, the D_{rd2} phase transforms into the I.L. phase at 197.0 °C at the intersection of the D_{rd2} phase line and the I.L. line, which is the clearing point of the D_{rd2} phase. Thus, this 'double clearing' behavior can be rationally explained by using the G–T diagram.

Since this double clearing behavior via the I.L. phase occurs for an enantiotropic relationship between D_{rd1} and D_{rd2}, it theoretically corresponds to Case B in the two types of double melting behavior reported previously.[21] Case A of double clearing behavior via an I.L. phase for a monotropic relationship between two discophases was reported recently.[22] Hence, Case B of double clearing behavior in the present work is the first example found, so far as we know.

3.4 The optical textures and the X-ray diffraction patterns of the two D_{rd} mesophases

The natural textures of these compounds (**2**, **3**, **4**) could be observed because they have an isotropic liquid (I.L.) phase although most of the phthalocyanine derivatives do not. The microphotographs of the textures of the metal-free derivative C_{12}–2H (**2c**) and the copper(II) com-

plex C_{12}–Cu (**4c**) are shown in Figs 3 and 4, respectively. Striated textures (Figs 3b and 4b) could be observed for the D_{rd1} mesophases at 150 °C of both the metal-free derivative (**2c**) and the copper(II) complex (**4c**). On the other hand, a mosaic texture (Fig. 3a) was obtained for the D_{rd2} mesophase of the copper(II) complex (**4c**) at 195 °C. The D_x mesophase of **2c** gave a 'leaf-like' texture.

Two kinds of D_{rd} mesophases of Cn–Cu (**4a**, **4b**, **4c**) could be further identified by a temperature-dependent X-ray diffraction technique. The X-ray diffraction data are summarized in Table 4. To date, four rectangular lattices for discotic mesophases have been reported, and these lattices have the characteristic extinction rules.[1,23] As can be seen from Table 4, each of the two mesophases was identified as a $D_{rd}(P2_1/a)$ mesophase. The symmetry of the two-dimensional rectangular lattice, $P2_{1/a}$, could be determined by the extinction rule; $h0$: $h=2n+1$; $0k$: $k=2n+1$. Although both the D_{rd1} and D_{rd2} mesophases peculiarly have the same $P2_1/a$ symmetry, they are not the same mesophase because they give different optical textures, as shown in Fig. 4.

The D_x mesophase in C_{12}–2H (**2c**) exists in too narrow a temperature region to employ the temperature-dependent X-ray diffraction technique. However, it is likely that the D_x mesophase is a $D_{rd2}(P2_1/a)$ mesophase, because the striated texture (Fig. 3b) is very similar to that (Fig. 4b) of the $D_{rd2}(P2_1/a)$ mesophase in C_{12}–Cu.

4 CONCLUSION

Eight novel octakis(3,4-dialkoxyphenyl)phthalocyanine derivatives, Cn–M (**2**, **3**, **4**), have been synthesized and characterized in this work. It was found that each of the derivatives is discogenic, and that each of the Cn–Cu (**4**) derivatives has two kinds of $D_{rd2}(P2_1/a)$ mesophases. These Cn–Cu (**4**) and C_{12}–2H (**2c**) derivatives exhibit an unusual double clearing behavior, which is the first example of such behavior in liquid crystals, so far as we know.

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