Preparation and Properties of Octaalkylphthalocyanines Having Long Alkyl Side Chains of Odd Numbers of Carbons

Hisao Nishi, Natsuhiro Azuma and Kiyoshi Kitahara*

Department of Applied Chemistry,
Faculty of Engineering, Saitama University,
Urawa 338, Japan

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2,3,9,10,16,17,23,23-Octaalkylphthalocyanines and their copper complexes having long alkyl side chains of odd numbers of carbons (C_7H_{12}, C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$) were prepared. Their thermal properties and solubilities were examined.

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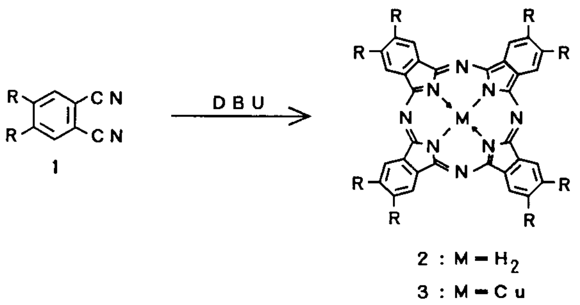
Phthalocyanines (Pcs) are attracting much attention as new functional materials, which are electronic devices and chemical sensors [1]. If we are planning to make use of the organic solids as functional materials, thin films using the Langmuir-Blodgett (LB) technique are the most interesting. However, the solubility of Pcs in organic solvents is very poor, so preparation of the LB films have been restricted. Solubilization of Pcs is successfully improved by introducing the bulky substituents such as alkylsiloxy [2], *tert*-butyl [3], *sec*-alkyl [4], alkoxy [5,7] and long alkyl groups [6,7], for restraint of intermolecular interaction. By the way, π-electron overlapping of Pcs in solid state influences the appearance of function [8]. In the case of the tetrasubstituted Pcs, geometrical isomer-production and separation of the products is difficult. We reported the synthesis and characterization of octaalkyl-Pcs having long alkyl groups of even number of carbons (R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$ and $C_{14}H_{29}$) [6]. These Pcs which kept molecular plane and symmetry in the LB films exhibited parallel orientation of the Pc macrocycle and electrochromism [9]. In this paper, we report the preparation and properties of octaalkyl-Pcs having long alkyl groups of an odd number of carbons (R = C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$).

Results and Discussion.

Scheme 1



	a	b	c	d
R	C_7H_{15}	C_9H_{19}	$C_{11}H_{23}$	$C_{13}H_{27}$

Phthalodinitrile derivatives **1** were prepared from *o*-dichlorobenzene in three steps [6,10]. Cyclization of **1** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave 2,3,9,10,16,17,23,24-octaalkyl-Pcs **2** or their copper complexes **3**. In the ^{1}H-nmr spectra, the signals of the N-H protons of **2** appeared as a singlet at δ -0.96 ~ -1.30 ppm. In the ir spectra of **2** and **3**, the absorptions of the alkyl groups and the phthalocyanine ring were observed. The elemental analysis confirms their molecular formula. In the electronic spectra, the characteristic uv (Soret band) and intense visible region (Q-band) absorptions of the Pc nucleus are well documented. Compounds **2** and **3** have a bathochromic shift of Q-band of about 10 nm compared with the unsubstituted Pc.

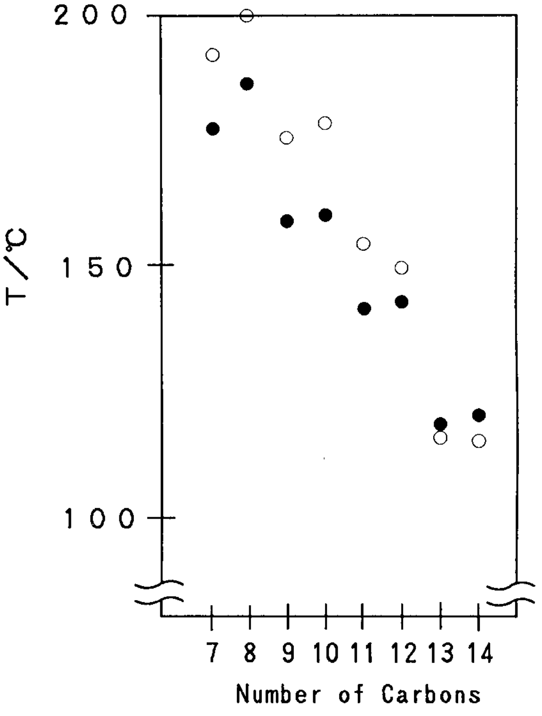


Figure 1. Transition temperatures (Tt) of **2** and **3**; ● : 2, ○ : 3

Compounds **2** and **3** were soluble in haloalkanes, aromatic hydrocarbons and halobenzenes, but insoluble in lower alcohols and acetone. The metal-free compounds **2** were more soluble than their copper complexes **3**. The heptyl derivative **2a** exhibited the highest solubility. In a previous paper [6], the solubility of the octaalkyl-Pcs having long alkyl groups of even number of carbons was much increased with the introduction of longer alkyl chains. There is a difference of the tendency between those of even and odd carbon atom alkyl groups.

In the thermal analysis of **2** and **3**, some phase transition temperatures were observed. Figure 1 shows the highest phase transition temperatures (Tt) of all of them. The Tt is lower with the introduction of longer alkyl chains on the whole. With regard to the phase transition temperatures as well as the solubility, however, there is a difference of the tendency between those of even and odd carbon atom alkyl groups. This result indicated that the odd-even effect was observed in the thermotropic liquid crystals which have a discotic structure [11,12].

EXPERIMENTAL

The ir, ms, and electronic absorption spectra were measured with a Perkin-Elmer FT-IR 1640, a Shimadzu QP-1000 and a Shimadzu UV-2100 spectrometers, respectively. The ^{1}H-nmr spectra were recorded with a JEOL PMX60Si and a Bruker AM-400 with TMS as the internal standard. Thermal properties were measured by the use of a Rigaku TG-DTA and a Seiko Denshi DSC. Solubility in chloroform at 20° was calculated from the molecular extinction coefficients [13,14].

Materials.

1,2-Dicyano-4,5-dialkylbenzenes **1** were prepared according to a known procedure [6]. 1,2-Dicyano-4,5-diheptylbenzene **1a** was a pale yellow liquid, yield 30%; ir (potassium bromide): 2956-2856 (C-H), 2232 ($C\equiv N$), 1466 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ 0.87 (t, J = 5.2 Hz, 6H, CH_3), 1.07-2.00 (m, 20H, C_5H_{10}), 2.67 (t, J = 8.5 Hz, 4H, CH_2), 7.47 (s, 2H, aromatic). 1,2-Dicyano-4,5-dinonylbenzene **1b** was a pale yellow liquid, yield 22%; ir (potassium bromide): 2956-2855 (C-H), 2233 ($C\equiv N$), 1466 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ 0.87 (t, J = 5.2 Hz, 6H, CH_3), 1.07-2.00 (m, 28H, C_7H_{14}), 2.63 (t, J = 8.5 Hz, 4H, CH_2), 7.43 (s, 2H, aromatic). 1,2-Dicyano-4,5-diundecylbenzene **1c** was a pale yellow liquid, yield 23%; ir (potassium bromide): 2955-2854 (C-H), 2233 ($C\equiv N$), 1466 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ 0.87 (t, J = 5.2 Hz, 6H, CH_3), 1.07-2.00 (m, 36H, C_9H_{18}), 2.63 (t, J = 8.5 Hz, 4H, CH_2), 7.47 (s, 2H, aromatic). 1,2-Dicyano-4,5-ditridecylbenzene **1d** was a pale yellow liquid, yield 38%; ir (potassium bromide): 2956-2856 (C-H), 2232 ($C\equiv N$), 1466 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ 0.87 (t, J = 5.2 Hz, 6H, CH_3), 1.07-2.00 (m, 44H, $C_{11}H_{22}$), 2.66 (t, J = 8.5 Hz, 4H, CH_2), 7.50 (s, 2H, aromatic).

2,3,9,10,16,17,23,24-Octaheptylphthalocyanine **2a**.

A solution of 1,2-dicyano-4,5-diheptylbenzene **1a** (0.50 g, 1.5 mmoles) and DBU (0.23 g, 1.5 mmoles) in 1-pentanol (5 ml) was refluxed under a nitrogen atmosphere for 20 hours. The precipitated blue solid was filtered, washed with dilute hydrochloric acid and water, and then recrystallized from mixed solvent of chloroform and hexane (1:1) to give dark blue powder of **2a** (0.12 g, 24%); ir (potassium bromide): 3290 (N-H), 2954-2852 (C-H), 1508, 1466, 1015 (H_2Pc, specific) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ = -1.26 (s, 2H, NH), 1.00 (t, 24H, CH_3), 1.33-1.86 (m, 64H, C_4H_8), 1.87-2.19 (m, 16H, CH_2), 3.13 (t, 16H, CH_2), 8.91 (s, 8H, aromatic); uv-vis (chloroform): λ max 295 (log ϵ 4.74), 343 (5.01), 611 (4.57), 648 (4.77), 673 (5.26), 708 (5.31); solubility in chloroform (20°): 7.0x10^{-4} mol/l.

Anal. Calcd. for $C_{88}H_{130}N_8$ (1300.1): C, 81.30; H, 10.08; N, 8.62. Found: C, 81.15; H, 9.95; N, 8.76.

2,3,9,10,16,17,23,24-Octanonylphthalocyanine **2b**.

The same procedure gave **2b** as a dark blue powder, yield 28%; ir (potassium bromide): 3290 (N-H), 2954-2851 (C-H), 1510, 1466, 1012 (H_2Pc, specific) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ = -1.20 (s, 2H, NH), 0.88 (t, 24H, CH_3), 1.15-1.80 (m, 96H, C_6H_{12}), 1.95-2.19 (m, 16H, CH_2), 3.21 (t, 16H, CH_2), 9.21 (s, 8H, aromatic); uv-vis (chloroform): λ max 294 (log ϵ 4.78), 344 (5.02), 610 (4.57), 651 (4.77), 672 (5.24), 708 (5.30); solubility in chloroform (20°): 1.9x10^{-5} mol/l.

Anal. Calcd. for $C_{104}H_{162}N_8$ (1524.5): C, 81.94; H, 10.71; N, 7.35. Found: C, 81.90; H, 10.52; N, 7.58.

2,3,9,10,16,17,23,24-Octaundecylphthalocyanine **2c**.

The same procedure gave **2c** as a dark blue powder, yield 27%; ir (potassium bromide): 3293 (N-H), 2955-2850 (C-H), 1507, 1466, 1012 (H_2Pc, specific) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ = -0.96 (s, 2H, NH), 0.88 (t, 24H, CH_3), 1.07-1.83 (m, 128H, C_8H_{16}), 1.90-2.17 (m, 16H, CH_2), 3.17 (t, 16H, CH_2), 9.05 (s, 8H, aromatic); uv-vis (chloroform): λ max 294 (log ϵ 4.79), 344 (5.02), 610 (4.56), 651 (4.77), 672 (5.25), 708 (5.31); solubility in chloroform (20°): 8.9x10^{-6} mol/l.

Anal. Calcd. for $C_{120}H_{194}N_8$ (1748.9): C, 82.41; H, 11.18; N, 6.41. Found: C, 82.14; H, 11.28; N, 6.21.

2,3,9,10,16,17,23,24-Octatridecylphthalocyanine **2d**.

The same procedure gave **2d** as a dark blue powder, yield 30%; ir (potassium bromide): 3294 (N-H), 2954-2850 (C-H), 1507, 1466, 1012 (H_2Pc, specific) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ = -1.30 (s, 2H, NH), 0.87 (t, 24H, CH_3), 1.05-1.85 (m, 160H, $C_{10}H_{20}$), 1.90-2.19 (m, 16H, CH_2), 3.12 (t, 16H, CH_2), 8.92 (s, 8H, aromatic); uv-vis (chloroform): λ max 295 (log ϵ 4.78), 344 (5.04), 609 (4.56), 650 (4.78), 672 (5.24), 708 (5.31); solubility in chloroform (20°): 7.6x10^{-6} mol/l.

Anal. Calcd. for $C_{136}H_{226}N_8$ (1973.3): C, 82.78; H, 11.54; N, 5.68. Found: C, 82.93; H, 11.50; N, 5.57.

2,3,9,10,16,17,23,24-Octaheptylphthalocyaninatocopper(II) **3a**.

A solution of 1,2-dicyano-4,5-diheptylbenzene **1a** (0.50 g, 1.5 mmoles), copper (I) chloride (0.053 g, .56 mmoles) and DBU (0.23 g, 1.5 mmoles) in 1-pentanol (5 ml) was refluxed under a nitrogen atmosphere for 20 hours. The precipitated blue solid was filtered, washed with dilute hydrochloric acid and water, purified by chromatography on alumina eluting with chloroform, and recrystallized from chloroform to give a dark blue powder **3a** (0.17 g, 32%); ir (potassium bromide): 2954-2853 (C-H), 1508, 1466, 1412 cm^{-1}; uv-vis (chloroform): λ max 293 (log ϵ 4.59), 342 (4.90), 619 (4.63), 688 (5.32); solubility in chloroform (20°): 1.5x10^{-4} mol/l.

Anal. Calcd. for $C_{88}H_{128}N_8Cu$ (1361.6): C, 77.63; H, 9.48; N, 8.23. Found: C, 77.37; H, 9.30; N, 8.28.

2,3,9,10,16,17,23,24-Octanonylphthalocyaninatocopper(II) **3b**.

The same procedure gave **3b** as a dark blue powder, yield 31%; ir (potassium bromide): 2954-2851 (C-H), 1508, 1467, 1412 cm^{-1}; uv-vis (chloroform): λ max 291 (log ϵ 4.63), 340 (4.89), 619 (4.61), 687 (5.32); solubility in chloroform (20°): 4.0x10^{-6} mol/l.

Anal. Calcd. for $C_{104}H_{160}N_8Cu$ (1586.0): C, 78.76; H, 10.17; N, 7.07. Found: C, 78.68; H, 10.07; N, 7.04.

2,3,9,10,16,17,23,24-Octaundecylphthalocyaninatocopper(II) **3c**.

The same procedure gave **3c** as a dark blue powder, yield 34%; ir (potassium bromide): 2954-2850 (C-H), 1508, 1466, 1412 cm^{-1}; uv-vis (chloroform): λ max 290 (log ϵ 4.78), 341 (4.95), 619 (4.63), 687 (5.32); solubility in chloroform (20°): 3.1x10^{-6} mol/l.

Anal. Calcd. for $C_{120}H_{192}N_8Cu$ (1810.4): C, 79.61; H, 10.69; N, 6.19. Found: C, 79.51; H, 10.90; N, 6.12.

2,3,9,10,16,17,23,24-Octatridecylphthalocyaninatocopper(II) **3d**.

The same procedure gave **3d** as a dark blue powder, yield 39%; ir (potassium bromide): 2954-2850 (C-H), 1508, 1467, 1412 cm^{-1}; uv-vis (chloroform): λ max 290 (log ϵ 4.68), 341 (4.93), 619 (4.62), 687 (5.32); solubility in chloroform (20°): 2.3x10^{-6} mol/l.

Anal. Calcd. for $C_{136}H_{224}N_8Cu$ (2034.9): C, 80.27; H, 11.10; N, 5.51. Found: C, 80.45; H, 11.17; N, 5.32.

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