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The title compounds were synthesized. They were soluble in organic solvents and their Q bands showed bathochromic shifts compared with unsubstituted 2,3-naphthalocyanines.

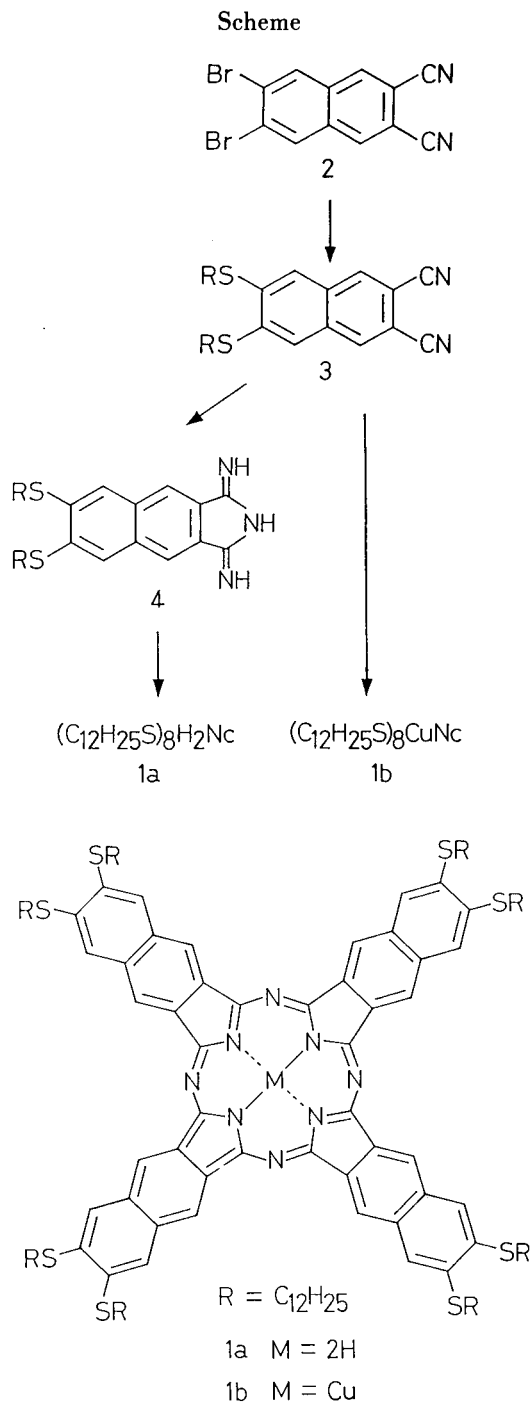
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Recently, naphthalocyanines (Nc) have become of interest in the family of phthalocyanines as an organic conductor [1] and near infrared dyes [2]. Nc were more insoluble than phthalocyanines. In assembling thin films of pigments by wet-process, *i.e.* the Langmuir-Blodgett technique, it is necessary for it to dissolve adequately in organic solvents. We have investigated the synthesis of soluble organic pigments which were phthalocyanine derivatives and carbazole dioxazine derivatives [3,4]. There are several reports on the synthesis of solvent-soluble Nc [5]. Soluble octa-substituted Nc, which have no geometrical isomers, have not been synthesized except 5,9,14,18,23,27,32,36-octasubstituted Nc [6]. We describe here the synthesis of 2,3,11,12,20,21,29,30-octadodecylthio-2,3-naphthalocyanine [(C<sub>12</sub>H<sub>25</sub>S)<sub>8</sub>H<sub>2</sub>Nc] (**1a**) and its copper(II) complex [(C<sub>12</sub>H<sub>25</sub>S)<sub>8</sub>CuNc] (**1b**).

Synthetic pathways to **1a,b** are summarized in the Scheme. Intermediate, 6,7-dibromonaphthalene-2,3-dicarbonitrile (**2**), was prepared in three steps starting from *o*-xylene modified to reference [7]. The condensation of **2** with 1-dodecanethiol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded 6,7-didodecylthio-naphthalene-2,3-dicarbonitrile (**3**). Since the 6 and 7 positions of **2** are activated by cyano groups, this reaction proceeded easily.

The synthesis of **1** employed the following two procedures. In the case of **1a**, **3** was converted into the corresponding 1,3-diiminobenz[*f*]isoindoline derivative **4** by reaction with sodium methoxide and ammonia in methanol. Compound **4** was used without purification because of its instability. Compound **4** in 1-pentanol and DBU was refluxed to afford green microcrystals of **1a**. The ir and <sup>1</sup>H-nmr of **1a** showed the NH stretching band and its protons, respectively. On the other hand, the copper complex **1b** was obtained by refluxing a mixture of **3**, copper(I) chloride, DBU and 1-pentanol [8]. The elemental analysis and electronic spectral data of **1a** and **1b** agree with their molecular formulas.

Compound **1** shows a strong single Q-band in the near infrared region as well as other naphthalocyanine series and has a bathochromic shift of Q-band (**1a**: 28 nm, **1b**: 24 nm) relative to unsubstituted 2,3-naphthalocyanines [9]. These compounds were soluble in aromatic hydrocar-



bones, aryl halides, haloalkanes and tetrahydrofuran. The solubility of **1a** and **1b** in chloroform at room temperature were  $1 \times 10^{-3}$  and  $7 \times 10^{-3}$  mole/l, respectively. The thermal behavior of **1** was evaluated by means of DSC and TG-DTA. Their thermograms exhibited endothermic peaks before decomposition (**1a**: 89, 98°, **1b**: 81°).

### EXPERIMENTAL

The ir, ms, nmr and electronic spectrum were recorded by means of a Perkin-Elmer FTIR-1640, a Shimadzu QP-1000, a JEOL PMX60Si/a Bruker AM400 and a Shimadzu UV-2100 spectrometers, respectively. Thermal properties were measured by the use of Rigaku TG-DTA and Seiko Denshi DSC.

#### Material.

6,7-Dibromonaphthalene-2,3-dicarbonitrile **2** [7] was prepared from 1,2-dibromo-4,5-bis(dibromomethyl)benzene and fumaronitrile. Compound **2** was pale yellow needles from DMF, yield 47%, mp >300° (sublimation).

#### 6,7-Didodecylthionaphthalene-2,3-dicarbonitrile **3**.

A mixture of **2** (435 mg, 1.29 mmoles), 1-dodecanethiol (652 mg, 3.22 mmoles), DBU (492 mg, 3.23 mmoles) and dry DMF 2 ml was heated 90° for 6 hours. After reaction, methylene chloride was added to the solution. The organic layer was washed with water, dried over magnesium sulfate and evaporated *in vacuo*. The residue was recrystallized from acetone to give yellow needles (486 mg, 65%), mp 105-106°; <sup>1</sup>H-nmr (carbon tetrachloride): 0.88 (t, 6H), 1.05-1.96 (m, 40H), 3.07 (t, 4H), 7.57 (s, 2H), 8.12 (s, 2H); ir (potassium bromide): 2230 cm<sup>-1</sup> (C≡N); ms: m/z 578 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>36</sub>H<sub>54</sub>N<sub>2</sub>S<sub>2</sub>: C, 74.68; H, 9.40; N, 4.84. Found: C, 74.65; H, 9.07; N, 4.80.

#### 2,3,11,12,20,21,29,30-Octadodecylthio-2,3-naphthalocyanine **1a**.

Anhydrous ammonia gas was bubbled through a stirred mixture of **3** (222 mg, 0.38 mmole), sodium methoxide (10 mg, 0.19 mmole) and dry methanol 2 ml for 1 hour. With continued ammonia introduction, the mixture was refluxed for 3 hours. After

the reaction, the solution was cooled and evaporated *in vacuo*. DBU (59 mg, 0.39 mmole) and 1-pentanol (1 ml) was added to the residue and refluxed for 6 hours. The precipitate was filtered off, washed with acetone, ethanol and water. Recrystallized from ethanol/chloroform (1:1) to give green microcrystals (84 mg, 38%), mp >290°; uv-vis (1-chloronaphthalene): λ max 358, 444, 808 nm; <sup>1</sup>H-nmr (deuteriochloroform at 45°): -1.50 (br s, 2H), 0.91 (t, 24H), 1.15-2.10 (m, 160H), 2.45-3.15 (br, 16H), 7.14 (br s, 8H), 7.87 (br s, 8H); ir (potassium bromide): 3280 cm<sup>-1</sup> (NH).

*Anal.* Calcd. for C<sub>144</sub>H<sub>218</sub>N<sub>8</sub>S<sub>8</sub>: C, 74.62; H, 9.48; N, 4.83. Found: C, 74.27; H, 9.36; N, 4.71.

#### 2,3,11,12,20,21,29,30-Octadodecylthio-2,3-naphthalocyaninato copper(II) **1b**.

A solution of **3** (268 mg, 0.46 mmole), copper(I) chloride (15 mg, 0.15 mmole) and DBU (100 mg, 0.68 mmole) in 1-pentanol (2 ml) was refluxed for 10 hours. The precipitate was filtered off, washed with methanol, acetone, and water. It was recrystallized from chloroform/methanol (1:1) to give green microcrystals (113 mg, 41%), mp >300°C; uv-vis (1-chloronaphthalene): λ max 438, 800 nm.

*Anal.* Calcd. for C<sub>144</sub>H<sub>216</sub>N<sub>8</sub>S<sub>8</sub>Cu: C, 72.69; H, 9.15; N, 4.71. Found: C, 72.39; H, 8.82; N, 4.47.

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