

# Synthesis of near-infrared absorbed metal phthalocyanine with S-aryl groups at non-peripheral positions

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**ABSTRACT:** Phthalocyanines are used as various applications, including as organic charge carriers in photocopiers, laser light absorbers in data storage systems, photoconductors in photovoltaic cells and electrochromic displays, and non-colored transparent film in visible region. The absorption maxima of phthalocyanines are best if moved near the infrared region for these applications. The Q band of phthalocyanines can be moved to bathochromic effects through extension of a  $\pi$  conjugation system such as naphthalocyanines and anthracyanines. Yields of naphthalocyanines and anthracyanines are, however, low. To solve the problem, novel metal phthalocyanines having non-peripheral *S*-aryl substituent were synthesized. The novel phthalocyanines show a high strain structure and no liquid crystal property. The target compounds were synthesized: 15 phthalocyanines from 2,3-dicyanohydroquinone in 3 steps *via* 1,2-dicyanobenzene-3,6-bis(trifluorate) and 1,2-dicyanobenzene-3,6-thiophenols. The Q bands of obtained compounds appeared in the near-infrared region. In particular, lead 1,4,8,11,15,18,22,25-octakis(thiophenylmethyl)phthalocyanine shows a Q band at 857 nm. Furthermore, non-colored transparent films in the visible region can be produced.

KEYWORDS: S-aryl substituent, near-infrared absorption, non-peripheral position.

# INTRODUCTION

Phthalocyanines, which are used as important greento-blue colorants, have attracted attention as functional chromophores for various applications including organic charge carriers in photocopiers, laser light absorbers in data storage systems, photoconductors in photovoltaic cells, electrochromic displays [1–6], and non-colored transparent films in the visible region. For these applications, absorption maxima of phthalocyanines, also called Q bands, are best if moved to the near-infrared region. The Q band absorption at around 650 nm is attributed to the  $\pi$ - $\pi$ \* transition. In general, the Q band of phthalocyanines can be moved to longer wavelengths through extension of  $\pi$  electron conjugation systems such as naphthalocyanines, anthracyanines and anthraquinocyanines [7]. For naphthalocyanines and anthracyanines, syntheses are difficult and yields are low. Therefore, it is necessary to continue investigate the synthesis of novel phthalocyanines of which the Q band shows near-infrared absorption, for example, to introduce an electron-donating substituent at a peripheral (2,3,9,10,16,17,13,24) position [1–6].

Cook and co-workers reported that 1,4,8,11,15,-18,22,25-octakis(hexylsulfanyl)phthalocyanines were moved in the Q band around 780 nm [8]. The substituents located at a non-peripheral (1,4,8,11,15,18,22,25) position can show bathochromic effects through comparison with the peripheral (2,3,9,10,16,17,23,24) position. Then, alkyl substituents in phthalocyanines linked through oxygen and sulfur atoms have the important effect of moving

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the Q band absorption to the near-infrared region: 760 and 800 nm [9, 10]. The wavelength of absorption maximum ( $\lambda_{max}$ ) of the Q band in 1,4,8,11,15,18,22,25octakis(hexylsulfanyl)phthalocyanine is dependent upon its central metal [8]. Especially, lead phthalocyanines show longer  $\lambda_{max}$  of the Q band because of their shuttlecock-shaped molecule. However, Cook's phthalocyanines were anticipated to show discotic liquid crystal behavior because of their long alkyl substitution. The phthalocyanines are thought to lack high heat resistance up to 300°C on a solid body. The Cook's phthalocyanines show red color because the Q band moved to the near-red region accompanying the Soret band [8].

In 2005, Kobayashi and co-workers reported synthesis of non-planar 1,4,8,11,15,18,22,25-octa(*p*-methoxyphenyl)phthalocyanines, of which the Q band was shifted beyond 800 nm [11]. Although most metal phthalocyanines have a planar structure, the bathochromic effect of the Q band observed for the octa(*p*-methoxyphenyl)phthalocyanines arises from ligand deformation and the electron-donating property of methoxy groups. Kobayashi's group also reported that 1,4,8,11,15,18,22,25-octaphenylated phthalocyanines have a high strain structure caused by the steric hindrance of substituents [12].

Near-infrared absorption materials were first reported in patents [12]. Infrared-absorbed phthalocyanines were obtained as a mixture of a constitutional isomer or regioisomers. The reason for the mixture of isomers is as follows: raw materials were added onto the mode of preparation of materials to decrease manufacturing processing; the selected molecular structures were unfortunately designed to include isomers and crude materials that cannot be easily separated into isomers. Even materials of the same series of phthalocyanine isomers are known to show different properties [13–16].

The authors reported a charge-transfer thin film made from organic varnish including aniline oligomer as a charge-transfer material exhibiting organic electroluminescent (EL) properties [17]. Copper phthalocyanine is used as a standard charge transfer material in the field of organic EL; it coats a surface with a thin film using a dry process such as a vacuum method because of the lower solubility of copper phthalocyanine. Copper phthalocyanine, having high heat resistance and high light resistance, is required for application to wet processes such as spin-coating, spraying, and ink-jet methods because of the demand for large EL display manufacture. Copper phthalocyanine presents the disadvantageous point of lower transmittance in the visible region because of its strong absorption maxima.

In this study, to develop new charge transfer materials, we attempt to synthesize novel non-peripheral *S*-aryl substituted phthalocyanines, 1,4,8,11,15,18,22,25octakis(thiophenyl)phthalocyanines, which show nearinfrared absorption, have high strain structure, with no liquid crystal property and no isomers, linking through sulfur atom electron-donating groups.

## **EXPERIMENTAL**

#### Equipments

Ultraviolet-visible (UV-vis) spectra were measured on a Shimadzu UV-2400PC spectrometer. Each sample was prepared in toluene at  $5.0 \times 10^{-5}$  M, and in chloroform at  $5.0 \times 10^{-5}$  M. Fluorescent spectra were recorded in DMF on a Nihon Bunko Jasco FP-6600 spectrofluorometer. Proton magnetic resonance (<sup>1</sup>H NMR) spectra were measured at 400 MHz on a Bruker Avance 400S in dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) using tetramethylsilane (TMS) as the internal standard. Elemental analysis was carried out using a Perkin-Elmer 2400CHN instrument. Mass spectra were taken with a Nihon Denshi Joel JMS-AX500 mass spectrometer. Melting points were measured with a stanford research system MPA100 optimelt automated system. A differential thermobalance was carried out using a MAC Science Tg-DTA 2000SR instrument. Measurement of the ionization potential (Ip) was performed using a Riken Keiki AC-2 instrument. Thickness of film was measured with a Kosaka Laboratories Suppercorder ET4000A instrument.

## Materials

All chemicals were purchased from Aldrich or Tokyo Chemical Industry Co. Ltd. They were used as received without further purification. For chromatographic separation, silica gel was used (60, particle size 0.063–0.200 nm, 7734-grade; Merck).

#### Synthesis

Phthalonitrile-3,6-ditriflate (1). 2,3-dicyanohydroquinone (4.80 g, 30 mmol) in dichloromethane (100 mL) and pyridine (py) (5.93 g, 75 mmol) was treated with trifluoromethanesulfonic anhydride (21.16 g, 75 mmol) under nitrogen at -78°C. After the reaction, the mixture was allowed to warm slowly to room temperature; stirring was continued for 24 h. The mixture was poured into water (600 mL) and the organic layer was extracted using dichloromethane ( $5 \times 100 \text{ mL}$ ). The extract was washed in turn with water, 2% hydrochloric acid, water, brine and water, and dried on magnesium sulfate (MgSO<sub>4</sub>). The filtrate and the solvent evaporated. The crude product was recrystallized from dichloromethane to afford 1 (6.35 g, 50%) as colorless needles. Found: C, 28.32%; H, 0.48%; N, 6.59%. Calcd. for  $C_{10}H_2F_6N_2S_2O_6$ : C, 28.31%; H, 0.48%; F, 26.87%; N, 6.60%; O, 22.63%; S, 15.12%. IR (KBr): cm<sup>-1</sup> 3115 (v<sub>C-H</sub>), 2550 (v<sub>C-N</sub>), 1601 (v<sub>C-C</sub>), 1472  $(v_{C-C})$ , 1439  $(v_{C-C})$ , 1134  $(v_{S=O})$ . <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ, ppm 8.44 (s, 2H).

**3,6-bis(thiophenyl)phthalonitriles (2).** In a mixture of **1** (0.85 g, 2 mmol), potassium carbonate (1.16 g) and dimethyl sulfoxide (DMSO) (15 mL), thiophenols (4 mmol) such as *p*-toluenethiol, 4-methoxybenzenethiol and *tert*-butylthiophenol was added; the mixture was reacted

at room temperature for 24 h in nitrogen atmosphere. The reaction products were poured into water (300 mL), and the organic layer extracted using dichloromethane  $(5 \times 100 \text{ mL})$ , and dried on MgSO<sub>4</sub>. The filtrate and the solvent evaporated. The crude product was washed with methanol  $(3 \times 50 \text{ mL})$  and recrystallized from toluene to afford **2** as a yellow solid. 3,6-bis(thiophenylmethyl) phthalonitrile (2a) (0.27 g, 35%). Found: C, 70.90%; H, 4.30%; N, 7.50%. Calcd. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>: C, 70.93%; H, 4.33%; N, 7.52%; S, 17.22. IR (KBr): cm<sup>-1</sup> 3050 (v<sub>C-H</sub>), 2970 (v<sub>C-H</sub>), 2218 (v<sub>C-N</sub>), 1600 (v<sub>C-C</sub>), 1535 (v<sub>C-C</sub>), 1490 ( $\nu_{C-C}$ ), 1435 ( $\nu_{C-C}$ ), 1210, 809 ( $\delta_{C-H}$ ). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ, ppm 7.54 (d, 4H), 7.46 (d, 4H), 7.35 (s2H), 2.66 (tt, 6H). 3,6-bis(thiophenylmethoxy)phthalonitrile (**2b**) (0.28 g, 34%). Found: C, 65.30%; H, 4.00%; N, 6.93%. Calcd. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>: C, 65.32%; H, 3.99%; N, 6.93%; S, 15.82%; O, 7.91%. IR (KBr): cm<sup>-1</sup> 3050  $(v_{C-H})$ , 2970  $(v_{C-H})$ , 2216  $(v_{C-N})$ , 1600  $(v_{C-C})$ , 1540  $(v_{C-C})$ , 1487 ( $v_{C-C}$ ), 1430 ( $v_{C-C}$ ), 1210, 810 ( $\delta_{C-H}$ ). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ, ppm 7.49 (d, 4H), 7.06 (d, 4H), 7.04 (s2H), 3.79 (s, 6H). 3,6-bis(thiophenyl *tert*-butyl)phthalonitrile (2c) (0.38 g, 42%). Found: C, 73.65%; H, 6.18%; N, 6.11%. Calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>S<sub>2</sub>: C, 73.64%; H, 6.18%; N, 6.13%; S, 14.04%. IR (KBr): cm<sup>-1</sup> 3040 (v<sub>C-H</sub>), 2960  $(v_{C-H})$ , 2210  $(v_{C-N})$ , 1600  $(v_{C-C})$ , 1500  $(v_{C-C})$ , 1460  $(v_{C-C})$ , 1210, 808 ( $\delta_{C-H}$ ). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$ , ppm 7.50 (d, 4H), 7.46 (d, 4H), 7.26 (s, 2H), 1.28 (s, 18H).

1,4,8,11,15,18,22,25-octakis(thiophenyl)phthalocyanines (3). A solution of 2 (0.25 mmol), metal chlorides or metal acetate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst and 1-pentanol (1-PeOH) was refluxed for 7 h. After cooling to room temperature, the reaction products were poured into methanol to form a precipitate, which was washed with water and methanol, and chromatographed on silica gel with toluene as eluent. 1,4,8,11,15,18,22,25-octakis(thiophenylmethyl)phthalocyanines (3a); 3a-Cu (0.02 g, 18%). Found: C, 67.98%; H, 4.51%; N, 7.01%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Cu: C, 67.99%; H, 4.21%; N, 7.21%; S, 16.50%; Cu, 4.09%. MS (FAB): *m*/*z* 1554, calcd. 1554.59. **3a-Co** (0.02 g, 24%). Found: C, 68.10%; H, 4.20%; N, 7.25%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>. S<sub>8</sub>Co: C, 68.19%; H, 4.23%; N, 7.23%; S, 16.55%; Co, 3.80%. MS (FAB): m/z 1550, calcd. 1549.97. 3a-Ni (0.03 g, 28%). Found: C, 68.18%; H, 4.20%; N, 7.13%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Ni: C, 68.20%; H, 4.23%; N, 7.23%; S, 16.55%; Ni, 3.79%. MS (FAB): m/z 1550, calcd. 1549.73. **3a-Zn** (0.02 g, 24%). Found: C, 67.87%; H, 4.23%; N, 7.11%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Zn: C, 67.91%; H, 4.21%; N, 7.20%; S, 16.48%; Zn, 4.20%. MS (FAB): m/z 1556, calcd. 1556.43. **3a-Pb** (0.04 g, 34%). Found: C, 62.29%; H, 3.88%; N, 6.40%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Pb: C, 62.24%; H, 3.86%; N, 6.60%, S, 15.11%; Pb, 12.19%. MS (FAB): m/z 1699, calcd. 1698.24. 3a-H<sub>2</sub> (0.04 g, 19%). Found: C, 70.85%; H, 4.66%; N, 7.51%. Calcd. for C<sub>88</sub>H<sub>66</sub>N<sub>8</sub>S<sub>8</sub>: C, 70.84%; H, 4.46%; N, 7.51%, S, 17.1%. MS (FAB): m/z 1492, calcd. 1492.04. 1,4,8,11,15,18,22,25-octakis-(thiophenylmethoxy)phthalocyanines(3b);3b-Cu(0.03g,

27%). Found: C, 62.88%; H, 3.91%; N, 6.65%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub> O<sub>8</sub>Cu: C, 62.82%; H, 3.89%; N, 6.66%; S, 15.25%; O, 7.61%; Cu, 3.77%. MS (FAB): m/z 1682, calcd. 1682.58. **3b-Co** (0.02 g, 21%). Found: C, 63.00%; H, 3.89%; N, 6.59%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>O<sub>8</sub>Co: C, 62.99%; H, 3.90%; N, 6.68%; S, 15.29%; O, 7.63%; Co, 3.51%. MS (FAB): m/z 1678, calcd. 1677.97. 3b-Ni (0.03 g, 25%). Found: C, 63.01%; H, 3.92%; N, 6.67%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>O<sub>8</sub>Ni: C, 63.01%; H, 3.92%; N, 6.67%; S, 15.29%; O, 7.63%; Ni, 3.49%. MS (FAB): m/z 1678, calcd. 1677.73. **3b-Zn** (0.03 g, 29%). Found: C, 62.75%; H, 3.95%; N, 6.65%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>O<sub>8</sub>Zn: C, 62.75%; H, 3.89%; N, 6.65%; S, 15.23%; O, 7.60%; Zn, 3.88%. MS (FAB): *m/z* 1684, calcd. 1684.42. **3b-Pb** (0.04 g, 35%). Found: C, 57.88%; H, 3.59%; N, 6.15%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>O<sub>8</sub>Pb: C, 57.88%; H, 3.59%; N, 6.14%; S, 14.05%; O, 7.01%; Pb, 11.33%. MS (FAB): *m*/*z* 1827, calcd. 1826.23. **3b-H**<sub>2</sub> (0.02 g, 8%). Found: C, 65.24%; H, 4.11%; N, 6.93%. Calcd. for C<sub>88</sub>H<sub>66</sub>N<sub>8</sub>O<sub>8</sub>S<sub>8</sub>: C, 65.24%; H, 4.11%; N, 6.92%, O, 7.90, S, 15.18%. MS (FAB): m/z 1620, calcd. 1620.03. 1,4,8,11,15, 18,22,25-octakis(thiophenyl tert-butyl)phthalocyanines (3c); 3c-Cu (0.02 g, 20%). Found: C, 71.13%; H, 6.05%; N, 5.87%. Calcd. for C<sub>112</sub>H<sub>113</sub>N<sub>8</sub>S<sub>8</sub>Cu: C, 61.13%; H, 6.02%; N, 5.92%; S, 13.56%; Cu, 3.37%. MS (FAB): *m*/*z* 1891, calcd. 1891.22. **3c-Co** (0.02 g, 21%). Found: C, 71.24%; H, 6.04%; N, 5.93%. Calcd. for C<sub>112</sub>H<sub>113</sub>N<sub>8</sub>. S<sub>8</sub>Co: C, 71.30%; H, 6.04%; N, 5.94%; S, 13.60%, Co, 3.12%. MS (FAB): m/z 1886, calcd. 1886.61. 3c-Ni (0.03 g, 23%). Found: C, 71.31%; H, 6.04%; N, 5.89%. Calcd. for C<sub>112</sub>H<sub>113</sub>N<sub>8</sub>S<sub>8</sub>Ni: C, 71.31%; H, 6.04%; N, 5.94%; S, 13.60%; Ni, 3.11%. MS (FAB): m/z 1886, calcd. 1886.37. 3c-Zn (0.03 g, 28%). Found: C, 71.00%; H, 6.01%; N, 5.92%. Calcd. for C<sub>112</sub>H<sub>113</sub>N<sub>8</sub>S<sub>8</sub>Zn: C, 71.06%; H, 6.02%; N, 5.92%; S, 13.55%; Zn, 3.45%. MS (FAB): m/z 1893, calcd. 1803.07. **3c-Pb** (0.04 g, 34%). Found: C, 66.12%; H, 5.63%; N, 5.53%. Calcd. for C<sub>112</sub>H<sub>113</sub>N<sub>8</sub>S<sub>8</sub>Pb: C, 66.11%; H, 5.60%; N, 5.51%; S, 12.61%; Pb, 10.17%. MS (FAB): *m/z* 2035, calcd. 2034.88. **3c-H**<sub>2</sub> (0.02 g, 9%). Found: C, 73.55%; H, 6.26%; N, 6.13%. Calcd. for C<sub>112</sub>H<sub>114</sub>N<sub>8</sub>S<sub>8</sub>: C, 73.56%; H, 6.28%; N, 6.13%, S, 14.03%. MS (FAB): m/z 1829, calcd. 1828.68.

**Reference compounds (4–6).** 1,4,8,11,15,18,22,25octakis(thiooctyl)phthalocyaninate copper, cobalt, nickel, zinc and lead (4) were synthesized from 3,6-thiooctylphthalonitrile in accordance with a description in the literature [4]. 2,3,9,10,16,17,23,24-octakis(thiophenylmethyl) phthalocyaninate copper, cobalt, nickel, zinc and lead (5) were synthesized from phthalonitrile having thiophenylmethyl at a peripheral site [18]. Tetrakis(*tert*-butyl)phthalocyaninate copper (6) was synthesized. **4-Cu.** Found: C, 73.90%; H, 7.65%; N, 4.76%. Calcd. for C<sub>144</sub>H<sub>177</sub>N<sub>8</sub>S<sub>8</sub>Cu: C, 73.91%; H, 7.62%; N, 4.79%; S, 10.96%; Cu, 2.72%. MS (FAB): *m*/z 2340, calcd. 2340.07. **4-Co.** Found: C, 74.06%; H, 7.64%; N, 4.77%. Calcd. for C<sub>144</sub>H<sub>177</sub>N<sub>8</sub>S<sub>8</sub>Co: C, 74.06%; H, 7.64%; N, 4.80%; S, 10.98%, Co, 2.52%. MS (FAB): *m*/z 2335, calcd. 2335.46. **4-Ni.** Found: C, 74.02%; H, 7.64%; N, 4.77%. Calcd. for C<sub>144</sub>H<sub>177</sub>N<sub>8</sub>S<sub>8</sub>Ni: C, 74.06%; H, 7.64%; N, 4.80%; S, 10.99%; Ni, 2.51%. MS (FAB): m/z 2335, calcd. 2335.22. 4-Zn. Found: C, 73.85%; H, 7.65%; N, 4.78%. Calcd. for C<sub>144</sub>H<sub>177</sub>N<sub>8</sub>S<sub>8</sub>Zn: C, 73.85%; H, 7.62%; N, 4.78%; S, 10.95%; Zn, 2.80%. MS (FAB): *m/z* 2342, calcd. 2341.92. **4-Pb.** Found: C, 69.63%; H, 7.18%; N, 4.41%. Calcd. for C<sub>144</sub>H<sub>177</sub>N<sub>8</sub>S<sub>8</sub>Pb: C, 69.63%; H, 7.18%; N, 4.51%; S, 10.32%; Pb, 8.35%. MS (FAB): m/z 2484, calcd. 2483.73. 5-Cu. Found: C, 68.00%; H, 4.28%; N, 7.29%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Cu: C, 67.99%; H, 4.21%; N, 7.21%; S, 16.50%; Cu, 4.09%. MS (FAB): m/z 1555, calcd. 1554.59. 5-Co. Found: C, 68.19%; H, 4.23%; N, 7.24%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Co: C, 68.19%; H, 4.23%; N, 7.23%; S, 16.55%; Co, 3.80%. MS (FAB): *m/z* 1550, calcd. 1549.97. **5-Ni.** Found: C, 68.21%; H, 4.24%; N, 7.21%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Ni: C, 68.20%; H, 4.23%; N, 7.23%; S, 16.55%; Ni, 3.79%. MS (FAB): m/z 1550, calcd. 1549.73. 5-Zn. Found: C, 67.89%; H, 4.19%; N, 7.24%. Calcd. for C88H65N8S8Zn: C, 67.91%; H, 4.21%; N, 7.20%; S, 16.48%; Zn, 4.20%. MS (FAB): m/z 1556, calcd. 1556.43. **5-Pb.** Found: C, 62.24%; H, 3.84%; N, 6.57%. Calcd. for C<sub>88</sub>H<sub>65</sub>N<sub>8</sub>S<sub>8</sub>Pb: C, 62.24%; H, 3.86%; N, 6.60%, S, 15.11%; Pb, 12.19%. MS (FAB): m/z 1699, calcd. 1698.24. 6-Cu. Found: C, 72.03%; H, 6.05%; N, 14.01%. Calcd. for C<sub>48</sub>H<sub>48</sub>N<sub>8</sub>Cu: C, 72.02%; H, 6.04%; N, 14.00%; Cu, 7.94%. MS (FAB): m/z 801, calcd. 800.49.

## **RESULTS AND DISCUSSION**

#### Syntheses of target compounds

Target compounds, 1,4,8,11,15,18,22,25-octakis(thiophenyl)phthalocyanines (**3**) were synthesized in three steps *via* intermediates, phthalonitrile-3,6-ditriflate (**1**) and 3,6-bis(thiophenyl)phthalonitriles (**2**). Intermediate **1**  was synthesized from 2,3-dicyanohydroquinon and trifluoromethanesulfonic anhydride for 24 h in accordance with a description from the literature [5]. Intermediates **2** were synthesized, respectively, from **1** and thiophenols such as *p*-toluenethiol, 4-methoxybenzenethiol and *tert*-butylthiophenol at room temperature for 24 h to obtain 3,6-bis(thiophenylmethyl)phthalonitrile (**2a**), 3,6-bis(thiophenylmethoxy)phthalonitrile (**2b**) and 3,6bis(thiophenyl *tert*-butyl)phthalonitrile (**2c**). Intermediates **1** and **2** were analyzed using IR and <sup>1</sup>H NMR spectroscopy, and elemental analysis. Their analytical data showed good agreement with the proposed structure.

The target compounds 1,4,8,11,15,18,22,25 octakis-(thiophenylmethyl)phthalocyanines (**3a**), 1,4,8,11,15,18,-22,25-octakis(thiophenylmethoxy)phthalocyanines (**3b**) and 1,4,8,11,15,18,22,25-octakis(thiophenyl *tert*-butyl) phthalocyanines (**3c**) were synthesized, respectively, from corresponding intermediates **2a**, **2b**, and **2c** and metal salt in the presence of DBU as catalyst in 1-PeOH for 7 h (Scheme 1). As metal salts, chloride or acetate of copper, cobalt, nickel, zinc, and lead were chosen [12]. Metalfree compounds of **3** were obtained directly by refluxing **2** in 1-PeOH. The products were isolated using column chromatography on silica gel with toluene as eluent. The most readily apparent feature of the **3** compounds is their solubility in various solvents.

The target compounds **3** were analyzed using elemental analysis and MS spectroscopy. The analytical data showed good agreement with the proposed structure.

#### Syntheses of reference compounds

For comparison of properties, reference compounds of three types were also synthesized. One kind of reference compound included 1,4,8,11,15,18,22,25octakis(thiooctyl)phthalocyaninate copper, cobalt, nickel,



Scheme 1. Synthetic pathway of 1,4,8,11,15,18,22,25-octakis(thiophenyl)phthalocyanine



Scheme 2. Synthetic pathway of reference compound 4



M=Cu, Co, Ni, Zn, Pb

Scheme 3. Synthetic pathway of reference compound 5

zinc and lead (4) from 3,6-thiooctylphthalonitrile, in accordance with a process described in the literature [7] (Scheme 2).

Other reference compounds were 2,3,9,10,16,17, 23,24-octakis(thiophenylmethyl)phthalocyaninate copper, cobalt, nickel, zinc and lead (**5**) synthesized from phthalonitrile having thiophenylmethyl at peripheral site [15] (Scheme 3). The other reference compound was tetrakis(*tert*-butyl)phthalocyaninate copper (**6**), which included four regioisomers [19]. The tetra-*tert*-butyl phthalocyaninate copper was synthesized from 4-*tert*-butylphthalonitrile. The reference compounds were analyzed using elemental analysis and MS spectroscopy. The

analytical data showed good agreement of the proposed structure.

#### **UV-vis spectra**

In substituted metal and metal-free phthalocyanines, strong absorption is detected in the visible region between the 650 and 690 nm, termed the Q band, and in UV between 320 and 370 nm, called the Soret band. A typical value for the extinction coefficient ( $\epsilon$ ) of the Q band is around 10<sup>5</sup> cm<sup>2</sup>. mol<sup>-1</sup>.

The absorption spectra of synthesized compounds 3 show typical shapes for phthalocyanine analogs (Figs 1–3).



Fig. 3. UV-vis spectra of 3c

They also displayed strong absorption peaks in the visible region at around 800 nm. The strongest peaks in the visible region are assigned as the Q band, which were attributed to the allowed  $\pi$ - $\pi$ \* transition of the phthalocyanine ring. The Q band absorption of synthesized compounds **3** shifted by 100–150 nm to a longer wavelength in comparison to unsubstituted metal phthalocyanine and reference compounds. In the case of **3a**, absorption maxima are moved to longer wavelengths in the order of Co, Ni, Cu, Zn, and Pb. Compounds 3b and 3c show similar phenomena. In comparison to the same central metal, non-peripheral substituted phthalocyanines, **3a**, **3b**, and **3c** show longer wavelengths than peripheral substituted 5. Metal-free 3a, 3b, and 3c were also synthesized. The Q band absorption peaks of **3a**, **3b**, and 3c respectively appeared at longer wavelengths of 815, 820, and 816 nm. In general, metal-fee phthalocyanines show shorter wavelengths than corresponding metal phthalocyanines. Metal-free 3a, 3b, and 3c, which have remarkably bulky substituents, increase the distortion of the molecule because the four central cavities cannot be fixed. Then, the Q band of metal-free 3a, 3b, and 3c were not split. The Q band is known to split into two peaks for high symmetry; the splitting Q band decreases with decreasing symmetry. Metal-free 3a, 3b, and 3c display decreased symmetry as a result of the molecular distortion. We leave a detailed discussion about these phenomena of Q band of metal-free 3a, 3b and 3c for another opportunity. The Q band absorption data of phthalocyanines are presented in Table 1.

The Q band shifts depend upon the change in the electron distribution in the phthalocyanine ring caused by substituents and their position. These results suggest that the steric hindrance arising from the substituted S-aryl groups appears to be as significant as reported by Kobayashi and co-workers [12]. However, a difference of the Q band in **3** is low between substituents, methyl, methoxy and *tert*-butyl. In this case, electron-donating substituents only slightly affect the movement to a longer wavelength. Although the effect of the central metal on the energy of Q band is usually small [20], absorption maxima of **3** are moved to longer wavelengths, and apparently increase with the ionic radius of the central metal, particularly lead. Lead complexes of **3** showed amplified structural distortion.

Because non-peripheral *S*-aryl substituted phthalocyanines having lead as the central metal have an absorption band near 500 nm, **3a-Pb**, **3b-Pb**, and **3c-Pb** resembles a red solution; the other central metals of **3a**, **3b**, and **3c** show a slightly reddish solution.

#### Heat resistance test

The respective heat resistance characteristics of **3** and **4** were estimated using a differential thermobalance instrument (Tg-DTA 2000SR; Mac Science). Heat resistance testing was the following: the sample temperature was raised from 30 to 400 °C by 1 °C every 1 min; the temperature was recorded at a point to 5% weight less per 400 mg sample weight. The target compounds **3a**, **3b**, and **3c** exhibited high 5% weight less temperature around 300°C, whereas reference compounds **4** showed a very low temperature. Results show that **3a**, **3b** and **3c** possess

Solvent	Central metal	3a		3b		3c		4	5	
		$\lambda_{max}$ , nm	log ε	$\lambda_{max}$ , nm	log ε	$\lambda_{max}$ , nm	log ε	$\lambda_{max}$ , nm	$\lambda_{max}$ , nm	log ε
Chloroform	metal-free	815	5.22	820	5.33	816	5.08			
	Pb	857	5.09	862	5.13	855	4.89	818		
	Cu	805	5.20	808	5.17	805	5.29	783		
	Ni	788	4.74	790	4.97	787	5.00			
	Zn	795	4.92	795	5.01	789	5.18	782		
	Со	779	4.91	783	4.51	780	4.91			
Toluene	Pb	838	5.15	846	5.18	836	5.08		754	4.89
	Cu	791	5.01	796	5.06	790	5.01		716	4.96
	Ni	777	5.09	782	5.10	776	4.94		706	4.99
	Zn	792	4.20	790	4.34	782	4.86		715	5.11
	Со	775	4.71	778	4.89	774	4.89		708	4.70

Table 1. Q band absorption data of target compounds 3a, 3b and 3c and reference compounds

Table 2. The 5% weight less temperature for 3a, 3b and 3c, andreference compound 4

Table 3. Ionization potential for 3a, 3b and 3c, and reference compound 5

Central metal	3a	3b	3c	4
Pb	298	298	291	73
Cu	305	302	300	81
Ni	305	301	296	80
Zn	312	306	303	75
Со	303	301	299	78

Central metal	3a	3b	3c	5		
Pb	4.80	4.90	4.75	5.11		
Cu	4.65	4.78	4.64	4.98		
Ni	4.69	4.82	4.68	5.03		
Zn	4.66	4.80	4.66	5.01		
Co	4.70	4.84	4.70	5.05		

very high heat-resistance. All **3** compounds are able to use an organic device and a thin film coated onto a surface. The 5% weightless data are presented in Table 2.

Compounds **4** show behavior of anisotropic discshaped liquid crystals around 70°C because of their longer alkyl side chains. These phenomena have been reported for long alkyl group substituted phthalocyanines [1, 2, 21].

#### Preparation of thin films and their ionization potentials

Under a nitrogen atmosphere, 0.3 g of **3** was dissolved in 5.0 g of 1,3-dimethyl-2-imidazolidinone. Cyclohexanol (5.0 g) was added to the 1,3-dimethyl-2-imidazolidinonesolution to afford varnish (including 3% solid content). The varnish was spin-coated onto an indium tin oxide (ITO) glass basal plate, which was washed with ozone for 40 min until immediately before spin-coating. The spin-coated ITO glass basal plates were baked at 200°C for 10 min to obtain 30-nm-thick thin films. The thin film thickness was measured (Supercorder ET4000A; Kosaka Laboratory). Prepared thin films of **3** show no apparent color difference from the solution phase.

Varnish of compound **5** is difficult to prepare to the same composition of the solvent to manufacture for **3**. For preparation of thin films, the solvent 1,3-dimetyl-2-imidazolidinone is an efficacious solvent for solid content, while cyclohexanol acts as a poor solvent. The solubility in cyclohexanol of **5** was lower than that of **3**. Therefore, the poor solvent was changed to chloroform.

Non-peripheral substituted phthalocyanines show higher solubility than peripheral substituted phthalocyanine because **3a** and **5** have identical substituents at differing positions. By improving the poor solvent, 30-nm-thick thin films containing **5** can be made.

The Ip of thin films were measured (AC-2; Riken Keiki Co. Ltd.). In the case of **3**, *Ip* were varied for the central metal, and increased in the order of Cu, Zn, Ni, Co, and Pb, which were independent of the S-aryl group type: thiophenylmethyl, thiophenylmethoxy, and thiophenyl *tert*-butyl. In comparison to the same central metal of **3**, the tendency of *Ip* shows a similar value for **3a** and **3c**, and is apparently the highest for **3b**. Comparison with *Ip* of thin films shows that those of 3 are lower than those of 5 by 0.5 eV. Actually, Ip is known to be around 5.0 eV for usually used non-substituted copper phthalocyanine thin films. The Ip of copper phthalocyanine shows a similar value for the peripheral substituted phthalocyanine, such as 5. Because Ip means energy of Highest Occupied Molecular Orbital (HOMO), non-peripheral S-aryl substituted phthalocyanines have the highest HOMO energy. This result suggests that non-peripheral S-aryl substituted phthalocyanines 3 removed a barrier of charge transfer using the electrode.

## CONCLUSION

Phthalocyanines having S-aryl at non-peripheral position can be synthesized. Their strong absorption peaks in the visible region called the Q band show around 800 nm. The synthesized phthalocyanines have high solubility for organic solvents, high heat resistance without discotic liquid crystal behavior, no absorption in visible region, and a simple compound including no regio isomers.

Thin films of synthesized phthalocyanine on ITO were prepared. The Ip measurements show that those of **3** were lower than those of **5** and copper phthalocyanine by 0.5 eV. Synthesized phthalocyanines **3** were removed as a barrier to charge transfer using an electrode.

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