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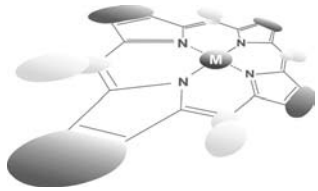

Synthesis and optical properties of tetrapyrazinoporphyrazines containing asymmetrical alkyl chains and *t*-butylphenyl groups

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ABSTRACT: Tetrapyrazinoporphyrazine magnesium complexes with four long alkyl groups and four 4-*tert*-butyl phenyl groups at the peripheral positions were synthesized from 2,3-dicyano-5-(4-*tert*-butylphenyl)-6-alkyl pyrazine derivatives using freshly prepared solutions of magnesium butoxide in *n*-butanol. The corresponding metal-free derivatives were obtained through treatment with *p*-toluenesulfonic acid. The resulting chromophores contained alkyl chains substituted at their peripheries and showed good solubility in organic solvents. The fluorescence of the tetrapyrazinoporphyrazine magnesium complexes was greatly influenced by the intermolecular aggregation. Q band spectra of the porphyrazine magnesium complexes in DMF exhibited the characteristic patterns of the monomeric species, with fluorescence maxima at 653–658 nm. These new compounds were characterized using UV-visible spectroscopy, MALDI-TOF-MS and ^{1}H NMR spectroscopy.

KEYWORDS: 2,3-dicyanopyrazine, tetrapyrazinoporphyrazine, *tert*-butyl group, fluorescence, spectral properties.

INTRODUCTION

Since Braun and Tscherniac first discovered phthalocyanine in 1907, many technological applications, such as optical disks, laser dyes, liquid crystals, electro-catalysts, and chemical sensors, have been investigated for these compounds [1, 2].

Unsubstituted metallophthalocyanines have intense colors but are generally insoluble in organic solvents or water, thereby limiting their use to just a few fields. The insolubility of the metal phthalocyanine derivatives is caused by molecular stacking, which is created by strong intermolecular interactions between the macrocycles in the phthalocyanine molecules. However, two methods can be used to improve the solubility in almost all solvents. The first method involves the use of a tri- or tetravalent transition metal as the core of the macrocycle, along with a coordination compound that contains an axial ligand from a central metal [3]. The second method involves the introduction of various peripheral substituents into the macrocycle [4, 5]. Bulky substituents sterically reduce the intermolecular π-π interactions, which minimizes the formation of aggregates, thereby improving solubility [6].

Like phthalocyanine, tetrapyrazinoprophyrazine is also a macrocycle ring system. It is a tetramerized structure of 2,3-dicyanopyrazine derivatives, which can be obtained in high yield by condensation of diaminomaleonitrile (DAMN) with various kinds of 1,2-diones. Similar to phthalocyanines, pyrazinoporphyrazines usually have Q bands under red region, and thus have similar areas of practical application. In addition, they have the same tendency of π-π interaction with macrocycles as phthalocyanines, so the same methods were researched to reduce aggregation.

Segregation between the rigid aromatic moieties and the flexible alkyl chains generally occurs for phthalocyanine

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macrocycles substituted with long alkyl chains, causing the formation of columnar mesophases. Therefore, the stability of phthalocyanine can be improved through the introduction of an adequate functional substituent at the peripheral positions of the phthalocyanine ring, which causes a substantial disruption in the strong interaction between the macrocycle rings. The increased stability expands the potential applications of phthalocyanines [7, 8].

On the other hand, the aggregation behavior of phthalocyanines is important because it decreases solubility and makes purification of the compound difficult. Furthermore, aggregation shortens the triplet-state lifetime and reduces the singlet oxygen quantum yield. Aggregation can be controlled using various techniques. For example, aggregation can be suppressed through the introduction of long alkyl chains or bulky substituents at the periphery of the phthalocyanine ring [9, 10]. Disaggregation behavior is exhibited in the basic condition because of the anionic effect, such as binding or deprotonation with the macrocycle ring. Phthalocyanines can be used as anion chemical sensors because of their optical changes.

The synthesis of functional dye materials based on 2,3-dicyanopyrazine chromophores was investigated, and the physical properties were correlated with their structures [11]. In this study, metal and metal-free tetrapyrazinoporphyrazines derived from 2,3-dicyano-5-(4-*tert*-butylphenyl)-6-alkyl pyrazine derivatives were designed and synthesized. This study focused on the change in the optical properties caused by the structure of the peripheral substituent, and the external conditions around the macrocycle.

EXPERIMENTAL

General

Flash chromatography was performed using a Merck-EM Type 60 (230–400 mesh) silica gel (flash). The ^{1}H NMR spectra were recorded using a VARIAN UnityInova 300 MHz FT-NMR spectrometer. UV-visible and fluorescence spectra were measured using Scinco S-4100 and Shimadzu RF-5301PC spectrophotometers, respectively. The MALDI-TOF-MS spectra were obtained using a Waters Limited MALDI-TOF spectrometer with dithranol as the matrix. The reagents and solvents used in the synthesis were all synthetic grade, and were used as received. The chemicals used for the spectroscopic analysis were all analytical reagent grade.

Typical procedure to synthesize 2a. Br_2 (40.0 g, 0.25 mol) was added dropwise to a solution of 4-(*tert*-butyl)butan-1-one derivative **1** (50.0 g, 0.25 mol) in 150 mL of $CHCl_3$ with stirring at 10 °C. After 2 h at room temperature, the mixture was diluted with ice water and extracted with 300 mL of dichloromethane. The organic layer was washed with water and dried with anhydrous sodium sulfate. The mixture was concentrated under a reduced pressure to form **2a** (yellow liquid, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 1.08 (t, J = 6.0 Hz, -CH_3, 3H), 1.36 (s, -*t*-Bu, 9H), 2.02–2.35 (m, -CH_2-, 2H), 5.14 (t, J = 7.5 Hz, Br-C-H, 1H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.99 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 11.73, 26.34, 31.16, 34.35, 54.51, 120.89, 124.10, 127.88, 152.53, 190.52. Anal. calcd. for $C_{14}H_{19}BrO$; C, 59.37; H, 6.76; Br, 28.21. Found C, 58.55; H, 6.69. **2b** (yellow liquid, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.89 (t, J = 6.0 Hz, -CH_3, 3H), 1.27 (br s, -CH_2-, 16H), 1.36 (s, -*t*-Bu, 9H), 2.02–2.31 (m, -CH_2-, 2H), 5.14 (t, J = 7.5 Hz, Br-C-H, 1H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.98 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.12, 22.72, 25.31, 28.64, 29.69, 31.30, 31.9, 34.23, 54.35, 124.90, 128.40, 133.61, 155.68, 191.20. Anal. calcd. for $C_{22}H_{35}BrO$; C, 66.82; H, 8.92; Br, 20.21. Found C, 66.81; H, 8.81. **2c** (yellow liquid, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.0 Hz, -CH_3, 3H), 1.26 (br s, -CH_2-, 16H), 1.34 (s, -*t*-Bu, 9H), 2.02–2.28 (m, -CH_2-, 2H), 5.14 (t, J = 7.5 Hz, Br-C-H, 1H), 7.50 (d, J = 9.0 Hz, Ar-H, 2H), 7.97 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.12, 22.72, 25.31, 28.65, 29.69, 31.30, 31.9, 33.02, 34.23, 54.35, 124.90, 128.40, 133.61, 155.70, 191.20. Anal. calcd. for $C_{24}H_{39}BrO$; C, 68.07; H, 9.28; Br, 18.87; O, 3.78. Found C, 68.24; H, 9.16.

Typical procedure to synthesize 3a. Brominated precursor **2a** (56.64 g, 0.2 mol) and potassium acetate (68.7 g, 0.7 mol) were refluxed in 200 mL of acetone. The solution was filtered and the solvent was removed *in vacuo*. The acetoxy group containing precursor was hydrolized in 60 mL of 10% NaOH in a methanol solution. After hydrolysis, the solution was filtered with methanol and extracted with 200 mL ethyl acetate and 250 mL of water. The organic layer was dried with sodium sulfate and evaporated *in vacuo*. The product was crystallized in *n*-hexane, and the resulting white crystal was filtered. **3a** (white crystal, 30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.90 (t, J = 6.0 Hz, -CH_3, 3H), 1.35 (s, -*t*-Bu, 9H), 1.67 (m, -CH_2-, 2H), 3.73 (s, -OH, 1H), 4.95 (s, -O-CH, 1H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.86 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 9.11, 24.37, 31.39, 34.27, 86.60, 124.89, 128.48, 131.13, 155.76, 197.02. Anal. calcd. for $C_{14}H_{20}O_2$; C, 76.33; H, 9.15; O, 14.52. Found C, 75.78; H, 9.34. **3b** (white crystal, 28%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.24 (br s, -CH_2-, 14H), 1.35 (s, -*t*-Bu, 9H), 1.52 (m, -CH_2-, 2H), 1.86 (t, J = 6.0 Hz, -O-C-CH_2, 2H), 3.73 (s, -OH, 1H), 5.05 (s, -O-CH, 1H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.86 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.12, 22.72, 24.81, 29.33, 29.61, 31.31, 31.92, 34.20, 84.40, 124.96, 128.40, 131.11, 155.76, 197.0. Anal. calcd. for $C_{22}H_{36}O_2$; C, 79.46; H, 10.91; O, 9.62. Found C, 79.16; H, 10.86. **3c** (white crystal, 31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.24 (br s, -CH_2-,

18H), 1.35 (s, -*t*-Bu, 9H), 1.52 (m, -CH_2-, 2H), 1.86 (t, J = 6.0 Hz, -O-C-CH_2, 2H), 3.73 (s, -OH, 1H), 5.05 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, -O-CH, 1H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.86 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.12, 22.72, 24.81, 29.34, 29.60, 31.31, 31.60, 31.92, 34.20, 84.40, 124.95, 128.40, 131.11, 155.76, 197.0. Anal. calcd. for $C_{24}H_{40}O_2$; C, 79.94; H, 11.18; O, 8.87. Found C, 79.74; H, 11.02.

Typical procedure to synthesize 4a. 1-(4-*tert*-butylphenyl)-2-hydroxybutan-1-one **3a** (18.06 g, 82 mmol) was added to a mixture of $CuSO_4 \cdot 5H_2O$ (42.5 g, 0.17 mol) in 42 mL of pyridine and 16 mL of water. The mixture was refluxed and monitored using thin-layer chromatography (TLC, ethyl acetate/*n*-hexane = 1/5). Then, the mixture was poured into 30 mL of a 10% HCl aqueous solution and 100 mL ice water and was vigorously stirred. After filtration, the filtrate was extracted with 200 mL ethyl acetate. The organic layer was dried with sodium sulfate, and the solvent was removed *in vacuo*. **4a** (yellow liquid, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.0 Hz, -CH_3, 3H), 1.34 (s, -*t*-Bu, 9H), 2.01 (s, -CH_2-, 2H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.92 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 8.21, 27.48, 31.32, 34.23, 125.54, 128.41, 129.52, 157.10, 190.49, 197.55. Anal. calcd. for $C_{14}H_{18}O_2$; C, 77.03; H, 8.31; O, 14.66. Found C, 77.08; H, 8.28. **4b** (yellow liquid, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.0 Hz, -CH_3, 3H), 1.26 (br s, -CH_2-, 14H), 1.34 (s, -*t*-Bu, 9H), 1.64–1.73 (m, -CH_2-, 2H), 2.86 (t, J = 7.5 Hz, -CH_2-, 2H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.92 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.11, 22.72, 24.81, 29.12, 29.30, 29.60, 31.31, 31.94, 34.25, 125.58, 128.48, 129.50, 157.17, 190.54, 197.53. Anal. calcd. for $C_{22}H_{34}O_2$; C, 79.95; H, 10.37; O, 9.68. Found C, 78.74; H, 10.01. **4c** (yellow liquid, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.26 (br s, -CH_2-, 18H), 1.34 (s, -*t*-Bu, 9H), 1.64–1.73 (m, -CH_2-, 2H), 2.86 (t, J = 7.5 Hz, -CH_2-, 2H), 7.51 (d, J = 9.0 Hz, Ar-H, 2H), 7.92 (d, J = 9.0 Hz, Ar-H, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.11, 22.72, 25.51, 29.12, 29.30, 29.60, 31.31, 31.94, 34.25, 125.58, 128.48, 129.50, 157.18, 190.54, 197.53. Anal. calcd. for $C_{24}H_{38}O_2$; C, 80.39; H, 10.68; O, 8.92. Found C, 80.41; H, 9.98.

Typical procedure to synthesize 5a. 1-(4-*tert*-butylphenyl)butane-1,2-dione **4a** (8.3 g, 38 mmol) was refluxed with 2,3-diaminomaleonitrile (4.09 g, 38 mmol) in 50 mL of methanol and amount of *p*-toluenesulfonic acid catalyst for 2 h. The reaction was monitored using TLC (ethyl acetate/*n*-hexane = 1/5). The solvent was removed *in vacuo* and the crude product was purified using column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/5 as the eluant). **5a** (yellow solid, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.38 (s, -*t*-Bu, 9H), 2.54 (s, -CH_2-, 2H), 7.57 (s, Ar-H, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 13.33, 29.01, 31.30, 34.23, 117.11, 125.42, 125.56, 129.94, 130.27, 131.31, 151.31, 158.15, 162.34. Anal. calcd. for $C_{18}H_{18}N_4$; C, 74.46; H, 6.25; N, 19.30. Found C, 73.38; H, 6.15; N, 18.84. **5b** (yellow solid, 36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.24 (br s, -CH_2-, 14H), 1.38 (s, -*t*-Bu, 9H), 1.71–1.81 (m, -CH_2-, 2H), 3.07 (t, J = 7.5 Hz, -CH_2-, 2H), 7.57 (s, Ar-H, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.13, 22.76, 29.20, 29.31, 29.67, 31.35, 31.90, 34.24, 34.31, 117.14, 125.48, 125.57, 129.94, 130.10, 133.0, 151.33, 159.12, 161.22. Anal. calcd. for $C_{26}H_{34}N_4$; C, 77.57; H, 8.51; N, 13.92. Found C, 77.64; H, 8.14; N, 13.89. **5c** (yellow solid, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.87 (t, J = 6.0 Hz, -CH_3, 3H), 1.24 (br s, -CH_2-, 18H), 1.38 (s, -*t*-Bu, 9H), 1.70–1.80 (m, -CH_2-, 2H), 3.05 (t, J = 7.5 Hz, -CH_2-, 2H), 7.56 (s, Ar-H, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 14.13, 22.76, 29.20, 29.31, 29.67, 31.35, 31.90, 34.24, 34.33, 117.10, 125.48, 125.57, 129.94, 130.10, 133.0, 151.33, 159.12, 161.21. Anal. calcd. for $C_{28}H_{38}N_4$; C, 78.10; H, 8.89; N, 13.01. Found C, 76.94; H, 8.34; N, 14.08.

Typical procedure to synthesize 6a. A suspension of Mg turnings (2 g, 0.08 mol), one small iodine crystal, and 150 mL of *n*-butanol was heated under reflux for 4 h. Then, the reaction mixture was cooled to room temperature and dicyanopyrazine **5a** (5.9 g, 0.02 mol) was added. The reaction mixture was quickly reheated to reflux, After approximately 10 min, the reaction mixture become dark green in color. After 1 h, the mixture was quenched through the addition of 200 mL of methanol and was filtered, The crude product was dark green and was purified using column chromatography with a silica gel as the stationary phase and chloroform/methanol (30/1) as the eluant. **6a** (dark green solid, 24%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 1.27 (broad s, CH_3, 12H), 1.57 (broad s, $C(CH_3)_3$, 36H), 3.66 (broad s, CH_2, 8H), 7.79 (broad s, Ar-H, 8H), 8.10 (broad s, Ar-H, 8H). UV-vis (log ε, $CHCl_3$): λ, nm 362 (4.90), 625 (4.52), 725 (4.41). Anal. calcd. for $C_{72}H_{72}MgN_{16}$: C, 72.93; H, 6.12; N, 18.90. Found: C, 71.07; H, 6.05; N, 18.74. MS (MALDI-TOF): *m/z* 1186.96 (calcd. 1185.75). **6b** (dark green solid, 26%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.95 (broad s, CH_3, 12H), 1.12–1.38 (broad m, methylene, 56H), 1.35 (broad s, $C(CH_3)_3$, 36H), 1.62 (broad s, Py-C-CH_2, 8H), 2.05 (broad s, Py-CH_2, 8H), 7.80 (broad s, Ar-H, 8 protons), 8.08 (broad s, Ar-H, 8 protons). UV-vis (log ε, $CHCl_3$): λ, nm 361 (4.94), 624 (4.62), 708 (4.55). Anal. calcd. for $C_{104}H_{136}MgN_{16}$: C, 76.42; H, 8.39; N, 13.71. Found: C, 75.88; H, 8.31; N, 13.64. MS (MALDI-TOF): *m/z* 1636.5 (calcd. 1634.6). **6c** (dark green solid, 20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.97 (broad s, CH_3, 12H), 1.20–1.57 (broad m, methylene, 72H), 1.38 (broad s, $C(CH_3)_3$, 36H), 1.70 (broad s, Py-C-CH_2, 8H), 2.25 (broad s, Py-CH_2, 8H), 7.80 (broad s, Ar-H, 8 protons), 8.10 (broad s, Ar-H, 8 protons). UV-vis (log ε, $CHCl_3$): λ, nm 361 (4.96), 625 (4.65), 708 (4.52). Anal. calcd. for $C_{112}H_{152}MgN_{16}$: C, 77.01; H, 8.77; Mg, 1.39; N, 12.83. Found: C, 76.31; H,

8.73; N, 11.99. MS (MALDI-TOF): *m/z* 1747.64 (calcd. 1746.82).

Typical procedure to synthesize 7a. *p*-toluenesulfonic acid (27.5 g, 0.16 mol) was added to a solution of Mg tetrapyrazinoporphyrazine (**6a**) (3.7 g, 3.1 mmol) in THF 100 mL, and the resulting mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*, leaving a dark green solid as the crude product, which was purified using column chromatography with a silica gel as the stationary phase and chloroform/methanol (30/1) as the eluant. **7a** (dark green solid, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm -1.47 (s, N-H, 2H), 1.51–1.54 (m, $C(CH_3)_3$, 36H), 1.69–1.75 (m, CH_3, 12H), 1.76–1.79 (m, CH_2, 8H), 7.74 (broad s, Ar-H, J = 9.0 Hz, 8H), 8.08 (m, Ar-H, J = 9.0 Hz, 8H). UV-vis (log ε, $CHCl_3$): λ, nm 345 (4.80), 628 (4.81), 661 (4.97). Anal. calcd. for $C_{72}H_{74}N_{16}$: C, 74.33; H, 6.41; N, 19.26. Found: C, 74.63; H, 6.32; N, 19.08. MS (MALDI-TOF): *m/z* 1164.84 (calcd. 1163.47). **7b** (dark green solid, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm -0.97 (s, N-H, 2H), 0.80–1.02 (m, CH_3, 12H), 1.05–1.43 (m, methylene, 56H), 1.50–1.55 (m, $C(CH_3)_3$, 36 protons), 2.16–2.40 (m, Py-C-CH_2, 8 protons), 3.52–3.70 (m, Py-CH_2, 8H), 7.65–7.79 (m, Ar-H, 8 protons), 7.92–8.05 (m, Ar-H, 8 protons). UV-vis (log ε, $CHCl_3$): λ, nm 347 (4.83), 628 (4.84), 661 (4.96). Anal. calcd. for $C_{104}H_{138}N_{16}$: C, 77.47; H, 8.63; N, 13.90. Found: C, 77.24; H, 8.70; N, 13.75. MS (MALDI-TOF): *m/z* 1613.29 (calcd. 1612.32). **7c** (dark green solid, 38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm -0.90 (s, N-H, 2H), 0.82–0.98 (m, CH_3, 12H), 1.20–1.45 (m, methylene, 72H), 1.50–1.65 (m, $C(CH_3)_3$, 36H), 2.08–2.20 (m, Py-C-CH_2, 8H), 3.60–3.70 (m, Py-CH_2, 8H), 7.64–7.80 (m, Ar-H, 8H), 7.98–8.12 (m, Ar-H, 8H). UV-vis (log ε, $CHCl_3$): λ, nm 341 (4.71), 629 (4.57), 661 (4.61). Anal. calcd. for $C_{112}H_{154}N_{16}$: C, 78.00; H, 9.00; N, 13.00. Found: C, 75.90; H, 9.09; N, 12.65. MS (MALDI-TOF): *m/z* 1725.07 (calcd. 1724.53).

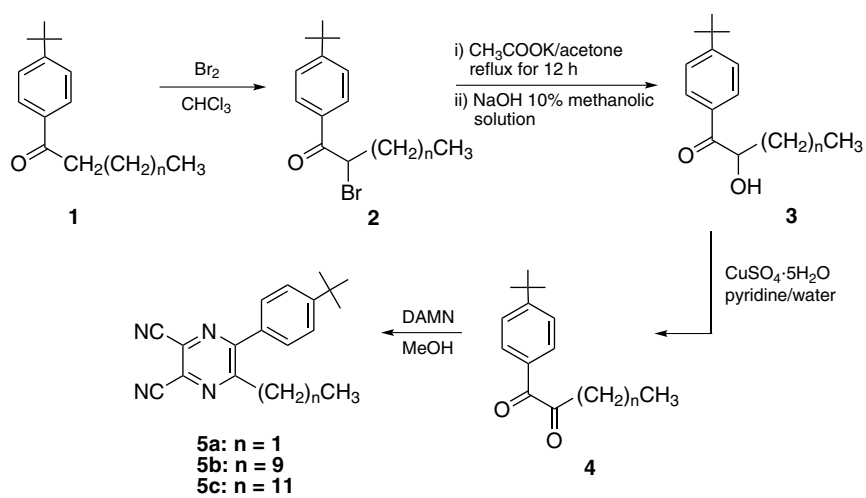
RESULTS AND DISCUSSION

Preparation of Mg and metal-free tetrapyrazinoporphyrazine compounds

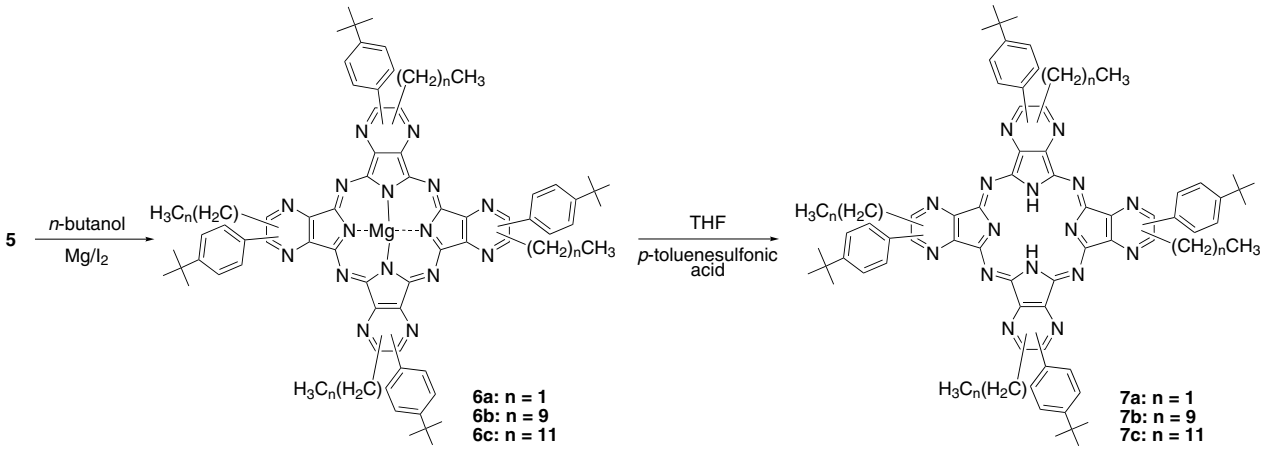
1-(4-*tert*-butylphenyl)butan-1-one (**1a**), 1-(4-*tert*-butylphenyl)dodecan-1-one (**1b**), and 1-(4-*tert*-butylphenyl)tetradecan-1-one (**1c**) were synthesized using the method described in previous literature [12]. These 4-(*tert*-butyl)alkylphenone derivatives **1** were treated with one equivalent of bromine in chloroform at room temperature to produce an 89–95% yield of α-brominated 4-(*tert*-butyl)alkyl phenone derivatives (**2**). The reaction of α-brominated ketones with an excess (2.8 equiv.) of anhydrous potassium acetate in acetone afforded α-acetoxylated 4-(*tert*-butyl)alkyl phenone [13, 14]. This compound was reacted with 10% methanolic NaOH under reflux conditions to produce the corresponding compounds of 1-(4-*tert*-butylphenyl)-2-hydroxybutan-1-one (**3a**), 1-(4-*tert*-butylphenyl)-2-hydroxydodecan-1-one (**3b**), and 1-(4-*tert*-butylphenyl)-2-hydroxytetradecan-1-one (**3c**). α-diketones **4** were obtained through the oxidation of α-hydroxyketones **3** with copper sulfate in aqueous pyridine solution. The dicyanopyrazine precursors **5** were synthesized from the condensation of α-diketones and 2,3-diaminomaleonitrile (DAMN) in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol. This reaction route is summarized in Scheme 1.

The final tetrapyrazinoporphyrazine magnesium complexes **6** were successfully synthesized using excess magnesium butoxide in *n*-butanol under reflux conditions. If required, these magnesium complexes were easily demetalated through stirring at room temperature for 30 min in excess amounts of *p*-toluenesulfonic acid in THF to produce **7** (in a yield range of 38–50%).

The chemical structures of the complexes are shown in Scheme 2. The structural assignments were established



Scheme 1. Reaction route of the tetrapyrazinoporphyrazine derivatives



Scheme 2. Reaction route of the magnesium and metal-free tetrapyrazinoporphyrazine complexes

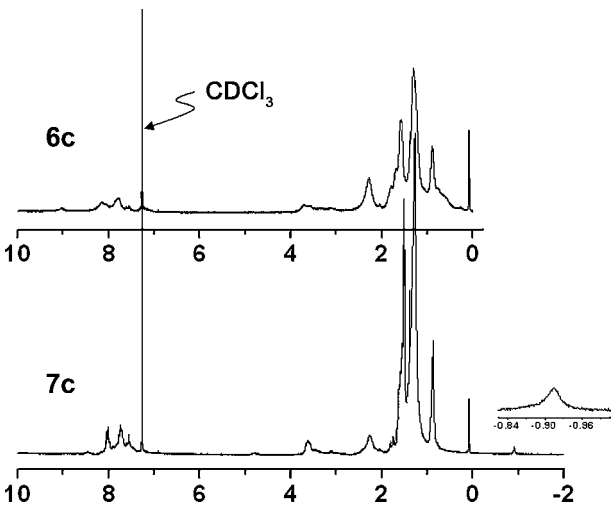


Fig. 1. ^{1}H NMR spectra of **6c** and **7c** in $CDCl_3$

based on MALDI-TOF mass, ^{1}H NMR, and UV-visible spectroscopy results.

In the MALDI-TOF MS spectra, tetrapyrazinoporphyrazines **6a** and **7a** displayed a single peak at *m/z* = 1185.75 (calcd. 1187.0) and 1163.47 (calcd. 1164.8), respectively, corresponding to $[M]^+$.

Figure 1 shows ^{1}H NMR spectra of **6c** and **7c**. Compared to **7**, a common feature of the proton NMR spectra for the tetrapyrazinoporphyrazinato magnesium complexes **6** was the relatively broad chemical shift attributed to the presence of aggregated species.

The ^{1}H NMR analysis of **6** and **7** showed the characteristic signals of both the *tert*-butyl group (-$C(CH_3)_3$, 0.97–1.57 ppm) and the aliphatic methyl group (-CH_3, 1.26–1.76 ppm) at an expected ratio of 3:1.

The aromatic protons of **7** appeared downfield between 7.75 and 8.09 ppm, whereas the chemical shift of the proton of inner nitrogen was observed from -0.90 to -1.47 ppm, much further downfield than phthalocyanine at -3.41 ppm. These downfield shifts were attributed to the electron-withdrawing effect of the pyrazine ring.

Spectroscopic characterization by UV-vis and fluorescence

Table 1 shows the absorption and fluorescence spectral data of tetrapyrazinoporphyrazines **6** and **7**. In chloroform, the absorption maxima in the visible spectra of **6** and **7** appeared between 625–705 nm because of the π-π* transition that is commonly referred to as the Q band. The B band (Soret band) was observed as a broad peak between 341–362 nm. The small broad area around the Q band region of **6** was attributed to structural mixtures resulting from their unsymmetrical structure. However,

Table 1. Absorption and fluorescence spectra of tetrapyrazinoporphyrazines

Compound	n	M	λ_{max}, nm[a]		F_{max}, nm	Φ_F[d]
			Soret band (B band)	Q band		
6a	1	Mg	362	625, 705	653[b]	0.63
6b	9	Mg	361	624, 708	654[b]	0.67
6c	11	Mg	361	625, 708	654[b]	0.74
7a	1	2H	345	628, 661	657[c]	0.39
7b	9	2H	347	628, 661	657[c]	0.44
7c	11	2H	341	629, 661	658[c]	0.48

[a] In chloroform. [b] Fluorescence maximum excited by 645 nm in DMF. [c] Fluorescence maximum excited by 628 nm in $CHCl_3$. [d] Measured by Williams method with Zn phthalocyanine.

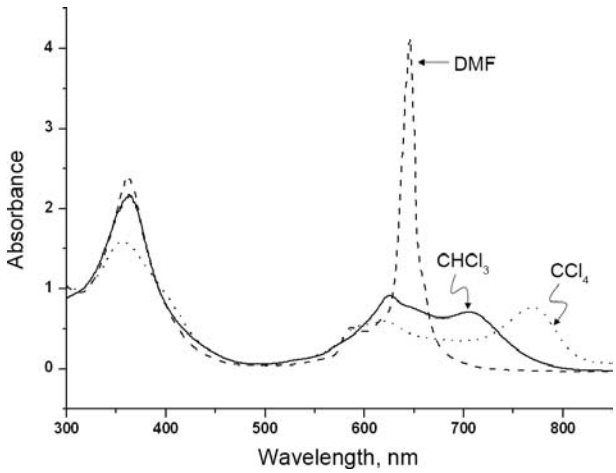


Fig. 2. The effects of the solvent polarity on the absorption spectra of **6a** (2.70×10^{-5} M)

the strange absorption curve observed in the chlorinated solvent was attributed to the molecular aggregation in the solution. Figure 2 shows the various changes in the absorption spectra depending on the solvent in arbitrary concentrations; the B band absorbances were matched to compare the Q bands.

Tetrapyrazinoporphyrazinato magnesium complexes (**6**) in *N,N*-dimethylformamide (DMF) showed red fluorescence with small Stoke's shift values. This indicates a high energy transformation efficiency for the absorbed light energy into the fluorescence. The fluorescence of **6a** was greatly influenced by the molecular aggregation. The Q band spectrum caused the first π-π* transition of **6** in DMF and showed a characteristic pattern of a monomeric species, with a fluorescence maxima at 653–658 nm. On the other hand, **6** in chloroform did not show any fluorescence and had the characteristic patterns of an aggregate (in Fig. 3).

The absorption spectra of the aggregate species exhibited a split Q band at 625 and 705 nm, which caused coupling of the transition moment between a pair (or more) of chromophores. Mizuguchi *et al.* reported that the molecular distortion of titanylphthalocyanine in a solid state produced a doubly degenerate excited level, causing split absorption bands [15]. The reduction of the molecular symmetry from the monomeric state to the dimeric state resolved the doubly degenerate level of the LUMO and gave two π-π* transitions which were orthogonal and on the molecular plane.

Visible absorption spectra of metal-free tetrapyrazinoporphyrazines (**7**) exhibited a well-resolved splitting of the Q_x/Q_y bands at 627–662 nm (in Fig. 4). The Q band spectra exhibited the characteristic patterns of a monomeric species with a strong red fluorescence. The absorption spectra of **6** in DMF did not have split Q_x/Q_y bands because of the electronic coupling between

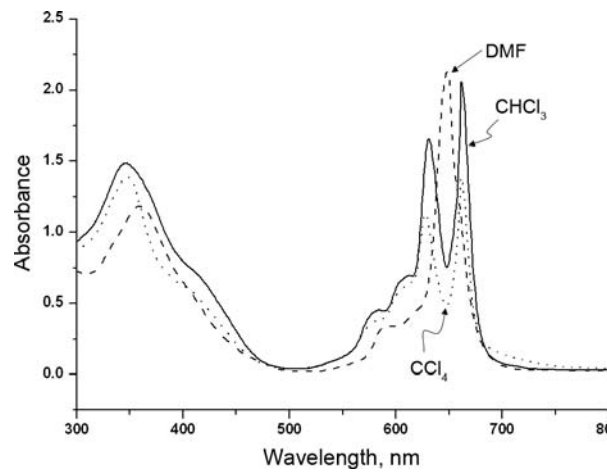


Fig. 4. The effects of the solvent polarity on the absorption spectra of **7a** (3.44×10^{-5} M)

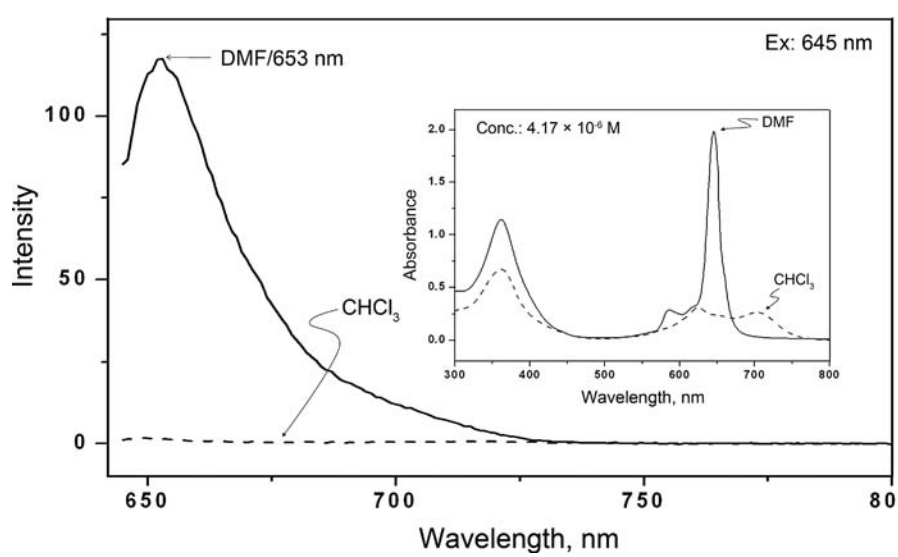


Fig. 3. Emission spectra of **6a** (4.17×10^{-6} M) in DMF and $CHCl_3$

a pair (or more) of porphyrazine units. However, the spectra recorded for the 10^{-5} and 10^{-6} M solutions of **7** in chloroform, carbon tetrachloride, and THF were identical in shape, implying that the aggregation was not very effective for metal-free porphyrazines **7** due to the bulky nature of the substituents that prevented the interaction between the porphyrazine cores at these concentrations.

Spectral change upon the addition of a base

A great deal of research has focused on the optical sensitivity of phthalocyanines because of their acid-base properties [16]. Figure 5 shows the UV-visible spectral changes of **6b** and **7b** upon the addition of tetrabutylammonium fluoride monohydrate (TBAF). Each of the Q band spectra contained a sharp peak, and the molar absorptivities of **6b** (λ_{max} = 647 nm, log ε = 4.76) were higher than the solutions without addition of TBAF. Previous research showed that the F^- anions can bind within the cores of metallophthalocyanines and form F^--coordinated complexes [17]. On the other hand, **7b** shows single peak of Q bands and the molar absorptivity (λ_{max} = 651 nm, log ε = 4.49) was decreased. It can be assumed that anions can cause the deprotonation of the pyrrole NH group of metal-free pyrazinoporphyrazines, leading to an optical change in metal-free tetrapyrazinoporphyrazine [18, 19].

Mg tetrapyrazinoporphyrazines exhibited no emission peaks in chloroform, but a strong emission peak was observed at around 600–700 nm when TBAF was added into the solution (Fig. 6). In contrast, unexpected results were observed in the metal-free porphyrazines. **7a**, **7b** and **7c** show the abnormal fluorescence quenching repeatedly. They show high PL in chloroform with no additive, and their emission disappeared when TBAF was added. In a previous study, the emission spectra of metal-free tetrapyrazinoporphyrazines typically had a

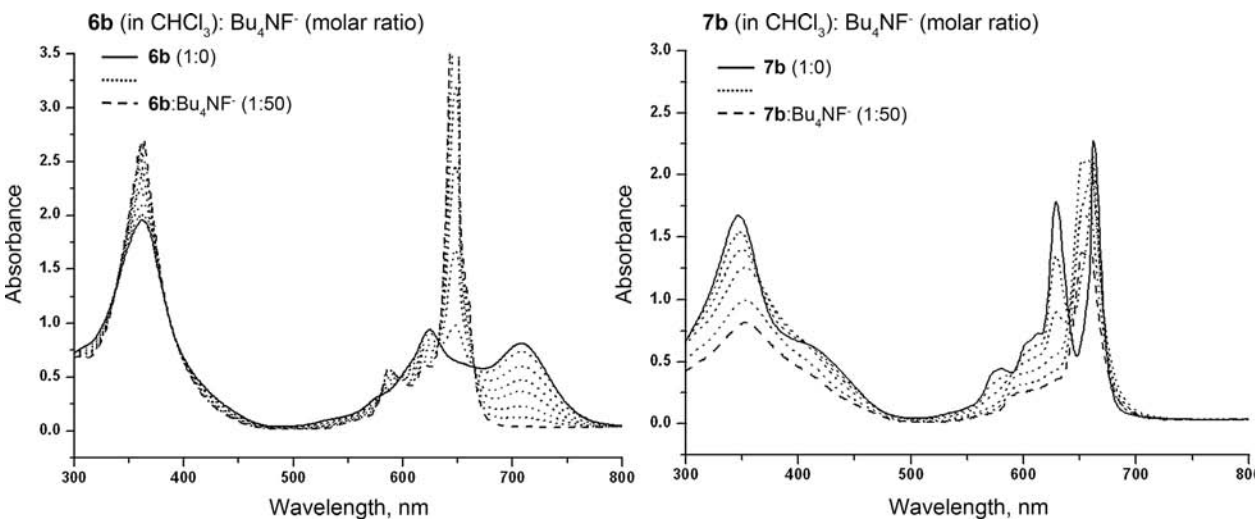


Fig. 5. Absorption spectral changes of **6b**, **7b** (7.0×10^{-5} M) with TBAF

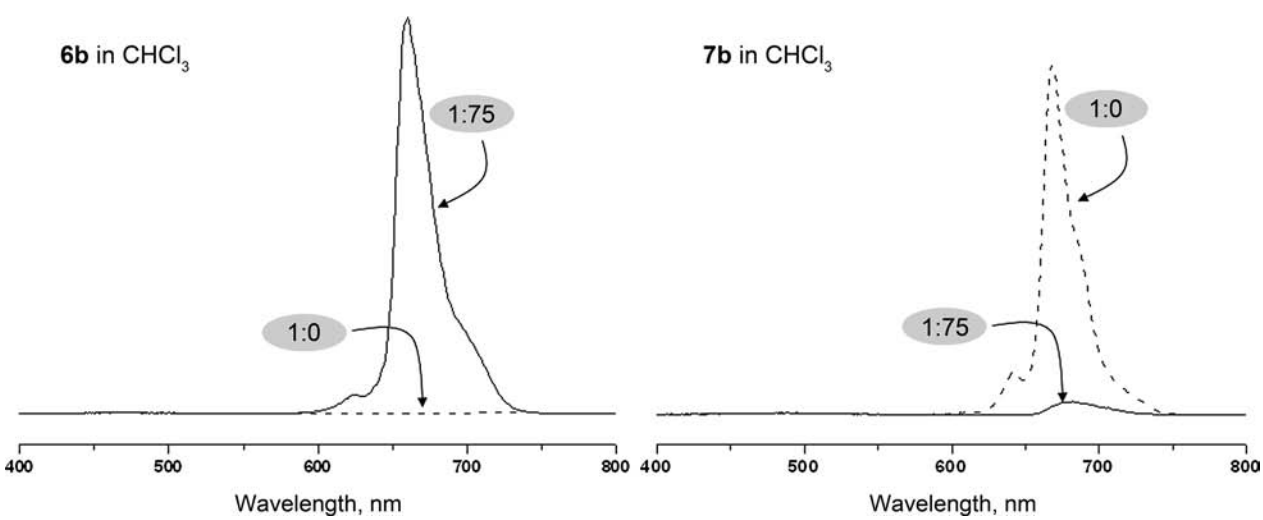


Fig. 6. The emission spectra of **6b**, **7b** (7.0×10^{-7} M) with TBAF (molar ratio)

Table 2. Tendencies of **6** and **7** under the condition of solution in chloroform

	6	**7**
No TBAF	Aggregated form	Monomeric form
	PL quenched	High PL
Addition of TBAF	Monomeric form	Aggregate-like form
	High PL	PL quenched

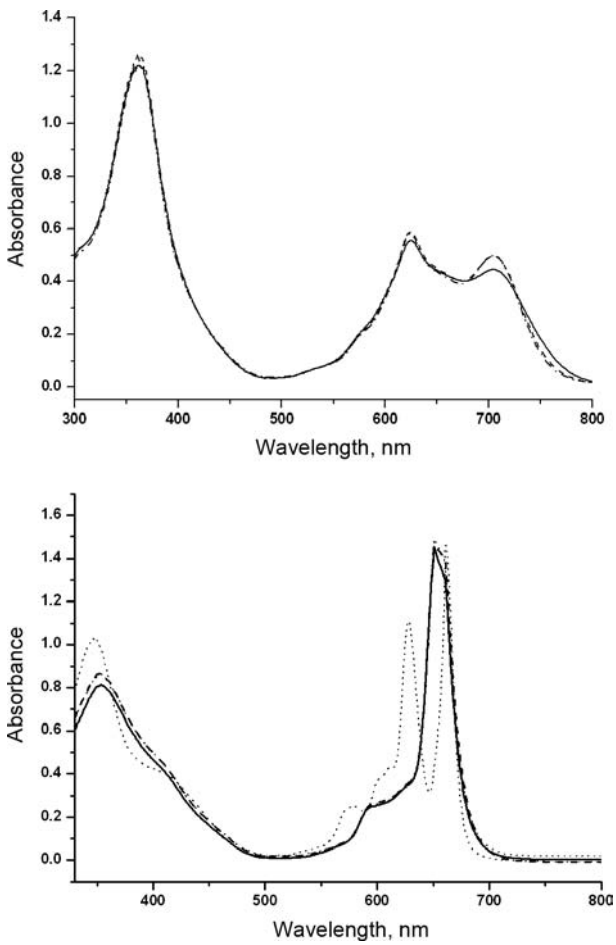


Fig. 7. UV-vis spectra of **6a** (no addition) and **7a** (with 1:75 molar ratio of TBAF) with different concentration

stronger photoluminescence than the pristine solution [20]. Table 2 summarizes the different tendency of **6**, **7** under the condition of solution in chloroform. Metal-free tetrapyrazinoporphyrazines show an optical tendency as an aggregated-like form of macrocycles. However, it is difficult to determine those phenomena as an aggregated form. Figure 7 shows UV-vis spectra of **6a** with no addition of TBAF, and **7a** with no addition of TBAF (dotted line) and 1:75 molar ratio of TBAF with different concentration (1.289×10^{-4} M in 0.1 cm cell (solid line), 1.289×10^{-5} M in 1 cm cell (solid line), 3.223×10^{-6} M in 4 cm cell (dash-dot line)). In the case of **7a**, the solid, dash and dash-dot lines were overlapped, indicating an optical change almost never occured due to the intermolecular interaction by concentration as shown in Fig. 7. Thus, we assumed it is more appropriate that this occurs as a result of the binding effect of the anion rather than from an aggregation effect between macrocycles. More investigation with regard to these phenomena will be carried out in further research.

CONCLUSION

In summary, we successfully synthesized organic-soluble tetrapyrazinoporphyrazines bearing long, linear alkyl and *tert*-butyl phenyl substituents at peripheral positions. Porphyrazines **6** and **7** have a satisfactory solubility in chlorinated hydrocarbons, THF, toluene, and *n*-hexane, but are practically insoluble in alcohols. Their UV-visible spectra show the typical shape of phthalocyanines, and this changed by solvatochromism due to the existence of different aggregated species.

Acknowledgements

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