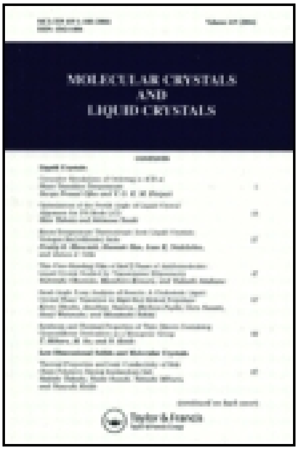

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Synthesis and Characterization of Novel Tetrapyrazinoporphyrazine Derivatives Containing Morpholine and tert-Butyl Group

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Version of record first published: 05 Oct 2009

To cite this article: Song Hak Kim, Do Kyung Lee, Chun Keun Jang, Seung Hwan Byun & Jae-Yun Jaung (2009): Synthesis and Characterization of Novel Tetrapyrazinoporphyrazine Derivatives Containing Morpholine and tert-Butyl Group, Molecular Crystals and Liquid Crystals, 509:1, 96/[838]-107/[849]

To link to this article: http://dx.doi.org/10.1080/15421400903054121

Mol. Cryst. Liq. Cryst., Vol. 509, pp. 96/[838]–107/[849], 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903054121

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Synthesis and Characterization of Novel Tetrapyrazinoporphyrazine Derivatives Containing Morpholine and *tert*-Butyl Group

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Tetrapyrazinoporphyrazine magnesium complexes were synthesized from 2,3-dicyano-5-(4-alkylphenyl)-6-(4-morpholinophenyl)pyrazine derivatives using freshly prepared solutions of magnesium butoxide in n-*butanol. The corresponding metal-free derivatives were obtained by treatment with* p-*toluenesulfonic acid. Copper complexes were successfully synthesized using excess cuprous chloride and DBU (1,8-diazabicyclo[5,4,0]-7-undecene) as a catalyst in* o-*dichlorobenzene under reflux. The tetrapyrazinoporphyrazines were characterized by elemental analysis, UV-visible spectra, IR, MALDI-TOF Ms and ^{1}H-NMR spectra.*

Keywords: 2,3-dicyanopyrazine; aggregation; bulky group; phthalocyanines; spectral properties

INTRODUCTION

Unsubstituted metallophthalocyanines have intense colors but are generally insoluble in both organic solvents and water, thereby limiting their use to just a few fields. It is well known that the insolubility

This study was supported by a grant from the Fundamental R&D Program (M200701004) for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy, and a grant No. R01-2006-000-10489-0 from the Basic Research Program of the Korea Science and Engineering Foundation and BK21 project in South of Korea.

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of such phthalocyanine derivatives results from their molecular stacking, which gives rise to strong intermolecular interactions between the macrocycles in the phthalocyanine molecules. When substituents are placed on the phthalocyanines ring, not only does the solubility of the compounds increase, but supramolecular organization can be achieved as well, with steric hindrance of the peripheral substituents reducing intermolecular π-π interactions. This effect minimizes the formation of aggregates, improving solubility. In the case of phthalocyanine macrocycles substituted with long alkyl chains, segregation between the rigid aromatic moieties and the flexible alkyl chains generally occurs, thereby resulting in the formation of columnar mesophases [1].

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. Tetrapyrazinoporphyrazine macrocycles tend towards higher aggregation compared to phthalocyanine molecules. A lot of aggregation inhibiting substituents have been developed as it is one of the most undesirable properties which decreases solubility, causes problems during purification, and shortens triplet state lifetimes crucial for the effects of tetrapyrazinoporphyrazines in photodynamic therapy [2]. These problems are usually solved through introduction of optimal substituents onto the periphery of the tetrapyrazinoporphyrazine core that suppress the aggregation.

2,3-Dicyanopyrazines for tetramerization (tetrapyrazinoporphyrazines) are usually built up through condensation of α-diketones and diaminomaleonitrile, enabling peripheral substitutions typically not available for phthalocyanines. Due to their interesting physical and chemical properties, tetrapyrazinoporphyrazines have been investigated in several applications [3]. Although they suffer from hypsochromic shifts (blue shift) compared to corresponding phthalocyanines, several types of peripheral substituents can induce important bathochromic shifts (red shift).

We have studied the syntheses of functional dye materials based on 2,3-dicyanopyrazine chromophores, and correlated their physical properties with structure [4]. In this paper, we synthesized novel, push-pull type pyrazine derivatives, bearing a morpholinophenyl substituent as an electron donor group at the 6-position, and cyano-substituents as electron acceptors at the 2- and 3-positions of pyrazine. We also designed and synthesized metal and metal-free tetrapyrazinoporphyrazines derived from 2,3-dicyano-5-(4-alkylphenyl)-6-(4-morpholinophenyl)pyrazine derivatives. Their aggregation behaviors, depending on solvent polarity, were correlated with their chemical structures.

EXPERIMENTAL

Compounds were identified and their properties were measured using the following techniques. Flash chromatography was performed with Merch-EM type 60 (230–400 mesh) silica gel (flash). Melting points were obtained with a capillary melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a VARIAN UnityInova 300 MHz FT-NMR spectrophotometer. UV-Vis spectra were measured using a SCINCO S-4100 spectrophotometer. MALDI-TOF-Ms (matrix-assisted laser desorption ionization time-of-flight mass) spectra were obtained on a Waters Limited MALDI-TOF spectrometer with dithranol as a matrix. Infrared spectra were taken on a MAGNA-IR 760 spectrometer using KBr pellets. Elemental analyses were performed with CE Instruments-EA 1110 Automatic Elemental Analyzer. All chemical were used of reagent grade without further purification unless otherwise specified.

1. 1-(4-Morpolinophenyl)-2-(4-tert-butylphenyl)ethan-1,2-Dione (1)

A mixture of 1-(4-bromophenyl)-2-(4-*tert*-butylphenyl)ethan-1,2-dione (1.72 g, 5 mmol), morpholine (0.65 g, 7.5 mmol), K_2CO_3 (1.38 g, 10 mmol), CuI (0.09 g, 0.5 mmol) and L-proline (0.11 g, 1 mmol) in 5 ml of DMSO was heated at 90°C for 21 hr. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel with ethyl acetate:hexane (1:3) as eluent. **1** (yellow solid, 56%); m.p.: 94–96°C; IR (KBr pellet): $v(\mathrm{cm}^{-1})$ 1677 (C=O); H-NMR (300 MHz, $CDCl_3$) δ: 1.36 (s, $-C(CH_3)_3$, 9 protons), 3.34–3.37 (t, CH_2, $J = 5.1$ Hz, 4 protons), 3.81–3.86 (t, CH_2, $J = 4.8$ Hz, 4 protons), 6.86 (d, Ar-H, J = 9.3 Hz, 2 protons), 7.50 (d, Ar-H, $J = 8.7$ Hz, 2 protons), 7.87 (d, Ar-H, J = 9.3 Hz, 2 protons), 7.91 (d, Ar-H, J = 6.9 Hz, 2 protons).

Elemental Anal. Calcd. For $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99; O, 13.66. Found: C, 75.16; H, 7.19; N, 3.90.

2. 1-(4-Tert-butylphenyl)-6-(4-morpholinophenyl)pyrazine-2,3-dicarbonitrile (2)

A solution of diketone (**1**) (1.0 g, 2.845 mmol), 2,3-diaminomaleonitrile (0.34 g, 3.186 mmol) and a small amount of *p*-toluenesulfonic acid as catalyst in methanol (10 ml) was refluxed for 2 hr. After the reaction was complete, the mixture was cooled at room temperature. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate:hexane (1:3) as eluent. **2** (yellow solid, 73%); m.p.: 183–186°C; IR (KBr pellet): $v(\mathrm{cm}^{-1})$ 2232 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.33 (s, -$C(CH_3)_3$, 9 protons), 3.26–3.29 (t, CH_2, $J = 4.8$ Hz, 4 protons), 3.83–3.86 (t, CH_2, $J = 5.1$ Hz, 4 protons), 6.79 (d, Ar-H, J = 9 Hz, 2 protons), 7.40 (d, Ar-H, $J = 8.7$ Hz, 2 protons), 7.55 (d, Ar-H, J = 8.7 Hz, 4 protons).

Elemental Anal. Calcd. For $C_{26}H_{25}N_5O$: C, 73.74; H, 5.95; N, 16.54. Found: C, 73.52; H, 5.80; N, 16.65.

3. Synthesis Tetrapyrazinoporphyrazine Metal Complexes

3.1. *Porphyrazine Magnesium Complex* (3)

Absolute *n*-buthanol was refluxed with magnesium (0.15 g, 6.17 mmol) and a small crystal of iodine for 4 hr, and then **2** (0.8 g, 1.54 mmol) was added and refluxing continued for next 3 hr. Aqueous acetic acid (50% (v/v), 50 ml) was added after evaporation of the solvent, and the suspension was stirred for 30 min. Dark solid was filtered and washed with aqueous acetic acid, water and methanol. Crude **3** was purified by column chromatography over silica gel with chloroform:methanol (50:1) as eluent. **3** (dark green powder, 38%); m.p. > 300°C; IR (KBr pellet): $v(\mathrm{cm}^{-1})$ 1300 (isoindole ring); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.53 (broad s, -$C(CH_3)_3$, 36 protons), 3.06–4.27 (m, CH_2, 32 protons), 7.06 (broad s, Ar-H, 8 protons), 7.61–8.16 (broad m, Ar-H, 24 protons).

Elemental Anal. Calcd. For $C_{104}H_{100}MgN_{20}O_4$: C, 72.69; H, 5.87; N, 16.30. Found: C, 72.57; H, 5.71; N, 16.07; MALDI-TOF-Ms spectra: m/z 1718.8 (calcd. 1718.34).

3.2. *Porphyrazine Copper Complex* (4)

A mixture of **2** (1.22 g, 2.82 mmol), CuCl (0.44 g, 4.53 mmol), and a catalytic amount of DBU (1,8-diazabicyclo[5,4,0]-7-undecene) in 12 ml *o*-dichlorobenzene was heated at 180–200°C for 6 hr. The deep greenish solution product was cooled to room temperature. The precipitate was washed with 5% HCl aqueous solution and ammonia solution. The solid product was washed with ethyl acetate and acetone and methanol, repeatedly. The crude product was purified by column chromatography chloroform:methanol (30:1) as eluent. **4** (dark blue powder, 31%); m.p. > 300°C; IR (KBr pellet): $v(\mathrm{cm}^{-1})$ 1300 (isoindole ring); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.53 (broad s, –$C(CH_3)_3$, 36 protons), 3.35 (broad s, CH_2, 16 protons), 4.01 (broad s, CH_2, 16 protons); 7.08 (broad s, Ar-H, 8 protons), 7.98–8.01 (broad m, Ar-H, 24 protons).

Elemental Anal. Calcd. For $C_{104}H_{100}CuMgN_{20}O_4$: C, 71.07; H, 5.73; N, 15.94. Found: C, 71.00; H, 5.61; N. 15.81; MALDI-TOF-Ms spectra: m/z 1759.1 (calcd. 1757.58).

3.3. *Metal-Free Tetrapyrazinoporphyrazine* (5)

Magnesium phthalocyanines (**3**) (0.5 g, 0.272 mmol) was dissolved in 20 ml of chloroform and a solution of tetrahydrofuran (2.58 g, 13.6 mmol) of was added. Mixture was stirred for 30 min at room temperature. After this time, solvent was evaporated and resulting solid was washed with water, hot methanol, and hot acetone. The crude product was purified by column chromatography chloroform:methanol (50:1) as eluent. **5** (dark blue powder, 45%); m.p.: 235–241°C; IR (KBr pellet): $v(\mathrm{cm}^{-1})$ 1300 (isoindole ring); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: -0.72 (s, N-H, 2 protons), 1.24 (s, $-C(CH_3)_3$, 36 protons), 3.11–3.35 (m, CH_2, 16 protons), 3.74–3.93 (m, CH_2, 16 protons), 6.93–6.99 (broad m, Ar-H, 8 protons), 7.43–7.53 (broad m, Ar-H, 8 protons), 7.94–8.00 (broad m, Ar-H, 16 protons);

Elemental Anal. Calcd. For $C_{104}H_{102}N_{20}O_4$: C, 73.65; H, 6.06; N, 16.52. Found: C, 73.49; H, 5.98; N, 16.41; MALDI-TOF-Ms spectra: m/z 1697.0 (calcd. 1696.05).

RESULTS AND DISCUSSION

1. Synthesis

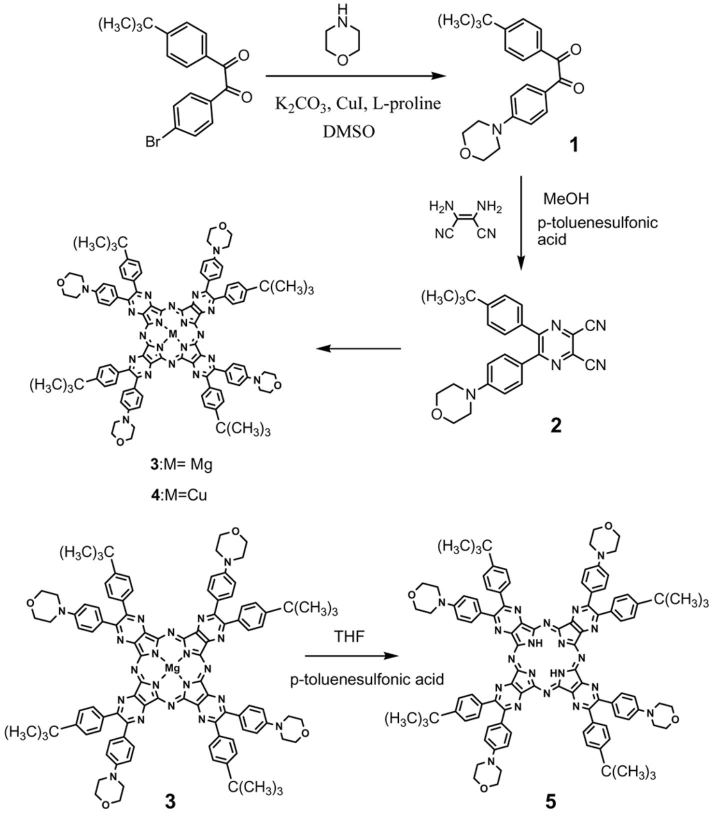
The 1-(4-bromophenyl)-2-(4-*tert*-butylphenyl)ethan-1,2-dione was synthesized by a method described in the literature [5].

CuI-catalyzed Ullmann-type reaction of electron-deficient aryl halides with aliphatic amines occurs at 40 ~ 90°C under the promotion of L-proline [6]. Using L-proline as the promoter, the coupling of 1-(4-bromophenyl)-2-(4-*tert*-butylphenyl)ethan-1,2-dione with morpholine (1.5 eq) in DMSO gave 1-(4-morpolinophenyl)-2-(4-*tert*-butylphenyl) ethan-1,2-dione in 56% yield.

However, due to the similar structure with phthalocyanine, synthesis of the tetrapyrazinoporphyrazines proceeded in a similar manner, prepared predominantly by cyclization reactions of substituted precursors of 2,3-dicyanopyrazines. The tetrapyrazinoporphyrazine precursor (**2**) was synthesized from reaction of the unsymmetrical α-diketone (**1**) and diaminomaleonitrile, in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol.

The tetrapyrazinoporphyrazine magnesium complexes (**3**) were successfully synthesized using excess magnesium butoxide in *n*-butanol under reflux. When required, these magnesium complexes were easily demetalated by stirring in excess *p*-toluenesulfonic acid, in THF, at room temperature, for 30 min, to produce **5** (in a yield range of 45 – 48%). Copper complexes (**4**) were also prepared by using excess cuprous chloride and DBU (1,8-diazabicyclo[5,4,0]-7-undecene) as a catalyst in *o*-dichlorobenzene at refluxing conditions. The synthetic route of this work is summarized in Scheme 1. The new compounds were characterized by FT-IR, UV-visible spectroscopy, MALDI-TOF-Ms, and ^{1}H-NMR spectroscopy.

From the FT-IR spectra of diketone (**1**) and dicyanopyrazine compound (**2**), the absorption band at 1677 cm^{-1} was characteristic of diketone, and the stretching vibrations of cyano group were also observed at 2232 cm^{-1}. The strong bands at 1300 cm^{-1} for **3** ~ **5** were characteristic of the isoindole ring, with a large contribution of the C-N stretching in the inner ring and the characteristic bands remaining.



SCHEME 1 Reaction routes of tetrapyrazinoporphyrazine derivatives.

Tetrapyrazinoporphyrazines **3** and **5** displayed a single peak at m/z = 1718.8 and 1697.0, respectively, corresponding to $[M]^+$ in the MALDI-TOF Ms spectra.

The ^{1}H-NMR spectra of tetrapyrazinoporphyrazines showed a broad peak in the corresponding range in $CDCl_3$ due to molecular aggregation, which is frequently encountered at concentrations used for NMR measurements. The proton absorption of the *tert*-butyl group was detected at 1.53 ppm in the ^{1}H-NMR spectrum of **3** and **4**, in $CDCl_3$. The inner NH protons of **5** are also very well characterized by ^{1}H-NMR, showing a peak at −0.72 ppm as a result of the magnetic anisotropy created by the 18 π-electron system of the phthalocyanine ring.

3.2. *Electronic Spectra and Aggregation Behavior*

Table 1 shows the maximum absorption wavelength and molar absorptivity (ε) values for tetrapyrazinoporphyrazines **3**, **4**, and **5** in $CHCl_3$. The ground state electronic spectra of the metal complexes showed characteristic absorption in the Q-band region at 665 nm for **3** and 669 nm for **4**. The B-band region was observed at 385 nm in $CHCl_3$. Compound **3** showed the highest molar absorptivity of all of the products. The B-bands were broaden due to the superimposition of the B_1 and B_2 bands. The Q-band, as well as the B-band, is a π-π^* transition [7].

The metal-free phthalocyanine gives a doublet (Q_x/Q_y) with Q-bands as a result of the D_{2h} symmetry [8]. However, the absorption spectra of **5** did not show split Q_x/Q_y bands, as shown in Figure 1, due to the electronic coupling between a pair (or more) of porphyrazine units [9].

The aggregation behavior of phthalocyanines is a specific property due to the intermolecular stacking of the planar and rigid core structures of the molecules. Tetrapyrazinoporphyrazine molecules become disaggregated through solvent polarity and bulky substituent groups [10,11]. The steric hindrance of the peripheral bulky *tert*-butyl group makes solubility possible in various organic solvents such as DMF,

TABLE 1 Absorption and Molar Absorptivity of Tetrapyrazinoporphyrazines of **3**, **4**, and **5** in $CHCl_3$ (1.94×10^{-5} M)

		λ_{max} (nm)		
Compd.	M	Soret band	Q-band	ε(l/mol·cm)
3	Mg	385	665	6.53×10^4
4	Cu	384	669	5.89×10^4
5	2H	386	683	4.62×10^4

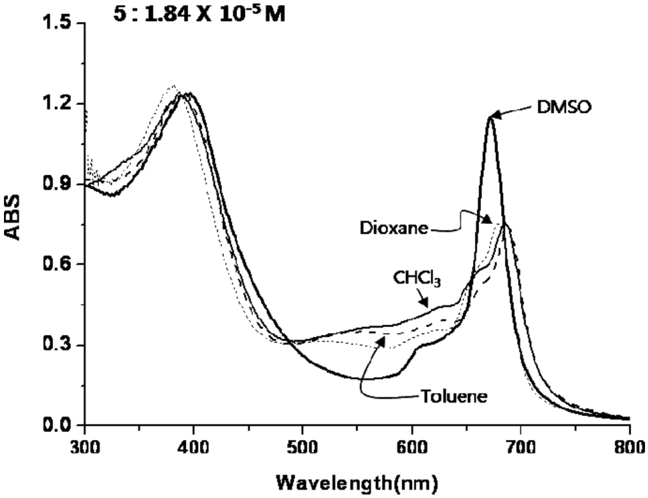


FIGURE 1 Absorption spectra of **5** in DMSO, $CHCl_3$, Toluene, and 1,4-dioxane.

DMSO, $CHCl_3$, THF, and 1,4-dioxane. While compounds **3** and **5** did not showed aggregation in DMSO, they did show aggregation in $CHCl_3$, 1,4-dioxane, and toluene, as judged by the broadening of the Q-band, Figures 1 and 2. DMSO is a strong coordinating solvent since they are known as the aggregation preventing solvent. And the change of the nature of a complexed ion in the cavity has an effect on the aggregative interaction [12]. Complex **4** did not show aggregation in 1,4-dioxane, but did show a broadness at 592 nm in $CHCl_3$, DMSO, and THF, suggesting aggregation (Fig. 3).

There has been a great deal of research focusing on the optical sensitivity of phthalocyanines due to their acidic and basic properties. The synthesized products also experienced an anion effect, especially with the F^-, Cl^-, OH^-, and CN^- anions, which were added to the non-aqueous solvents in the form of a tetra-*n*-butylammonium salt. Previous researchers indicated that it either forms F^--coordinated complexes [13] or causes deprotonation of the proton on the pyrrole group of metal-free phthalocyanines [14]. In our case, Figure 4 showed the UV-visible spectral changes of **3** and **5** in chloroform upon adding tetrabutylammonium fluoride monohydrate (TBAF). And another experiments of other anion case such as Cl^-, OH^-, and CN^- anions was also carried out in other solvent THF (Fig. 5).

As the synthesized tetrapyrazinoporphyrazines added the form of four tetra-*n*-butylammonium salts, the spectra of above anions were found to change rapidly. As stated above, it showed that the anions

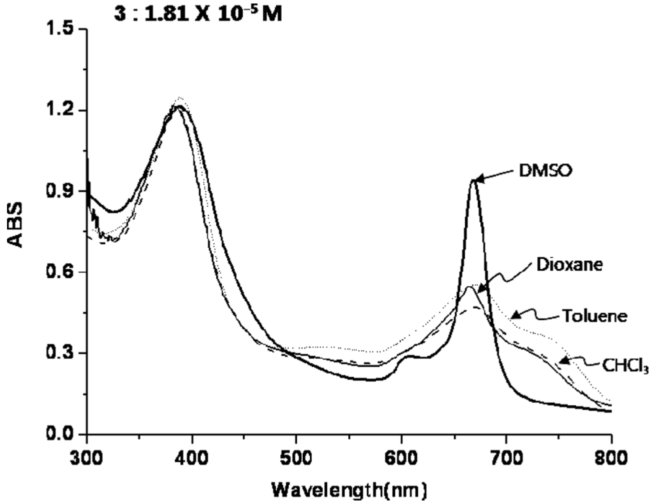


FIGURE 2 Absorption spectra of **3** in DMSO, $CHCl_3$, Toluene, and 1,4-dioxane.

could bind within the cores of the metallophthalocyanines. Isosbestic points were observed and equilibrium mixtures of the monomer and aggregate were included in the solution. The spectra showed a sharp peak in the Q-band and molar absorptivity was higher than that for the initial solution.

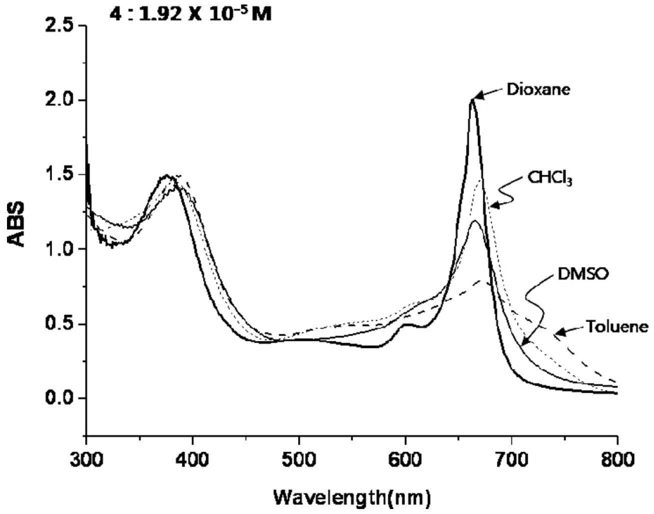


FIGURE 3 Absorption spectra of **4** in DMSO, $CHCl_3$, Toluene, and 1,4-dioxane.

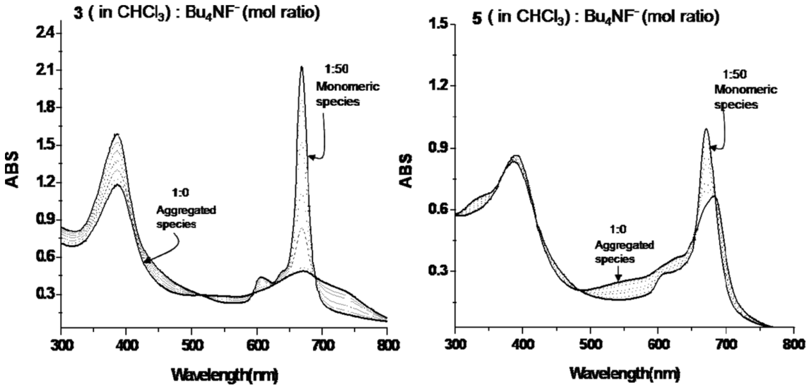
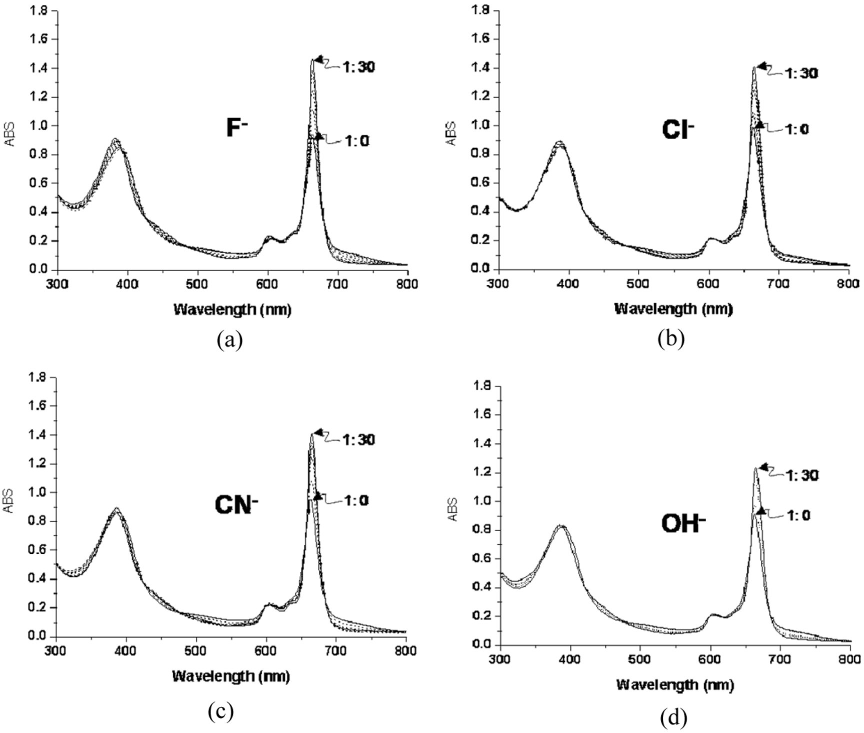


FIGURE 4 UV-visible absorption spectral change upon adding TBAF to **3** (1.84×10^{-5} M) and **5** (1.65×10^{-5} M).



(a)

(b)

(c)

(d)

FIGURE 5 UV-visible absorption spectral change upon adding anions (F$^-$, Cl$^-$, OH$^-$, and CN$^-$) to **3** in THF (1.51×10^{-5} M)

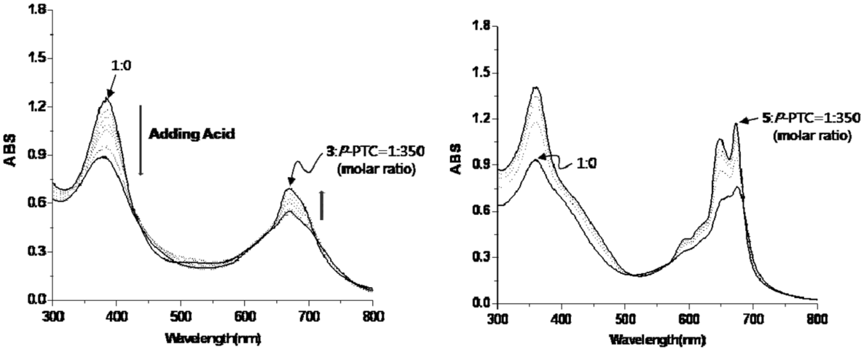


FIGURE 6 UV-visible spectral change adding upon an acid (*p*-toluenesufonic acid) to **3** (1.45×10^{-5} M) and **5** (1.65×10^{-5} M)

There has also been a great deal of research focusing on the optical sensitivity of phthalocyanines to acidic conditions. The UV-visible spectra of the synthesized tetrapyrazinoporphyrazines in chloroform: methanol (9:1) were measured by varying the mole ratio of tetrapyrazinoporphyrazines:*p*-toluenesulfonic acid, as shown in Figure 6. The addition of *p*-toluenesulfonic acid to the chloroform:methanol (9:1) solution of tetrapyrazinoporphyrazines resulted in reduction of aggregation as evidenced by the sharp increase in Q-band intensity. When the concentration of *p*-toluenesulfonic acid was increased, the absorption intensity of Q-band increased due to the electrostatic repulsion between the morpholino group of the tetrapyrazinoporphyrazines and the acidic group of the *p*-toluenesulfonic acid.

CONCLUSION

In summary, we designed and synthesized metal and metal-free tetrapyrazinoporphyrazines bearing a morpholinophenyl substituent as an electron donor group at the 6-position, and cyano-substituents as electron acceptors at the 2- and 3-positions of pyrazine.

Its UV-vis absorbance were announced by changing the environment of the molecule, for instance, organic solvent, acid, basic condition. The aggregation behavior is a typical phenomenon of phthalocyanines and the synthesized tetrapyrazinoporphyrazines also show aggregation due to intermolecular π-π interactions. In our case, the optical properties of tetrapyrazinoporphyrazine derivatives was changed in controlling the environment of the molecules through solvent polarity and bulky substituent groups. The synthesized products also experienced an anion effect containing the F^-, Cl^-, OH^-, and CN^- anions. As the synthesized tetrapyrazinoporphyrazines added the form of a tetra-*n*-butylammonium salt, the spectra were found to change rapidly. It shows that the chemical sensoring ability is acceptable for these molecules.

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