Synthesis of Organo-soluble Tetrapyrazinoporphyrazines and Their Visible Spectra Properties

Chun Keun Jang, Song Hak Kim, Do Kyung Lee, and Jae-Yun Jaung*

*Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, Korea. *E-mail: jjy1004@hanyang.ac.kr*
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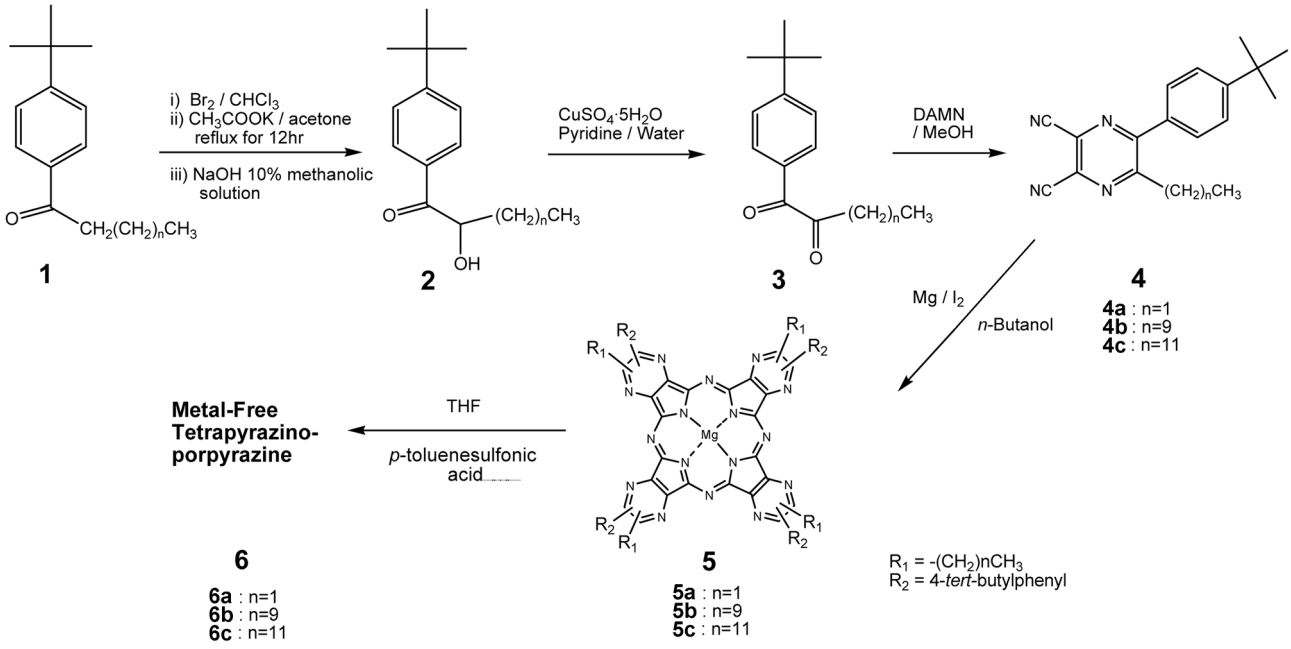
There were many researches about phthalocyanines for various applications such as chemical sensor,[1] catalyst,[2] etc. The unsubstituted metallophthalocyanines have intense colors but are generally insoluble in organic solvents or water, thereby limiting their use to just a few fields. It is well known that the insolubility of metal phthalocyanine derivatives results from their molecular stacking, which gives rise to strong intermolecular interactions between the macrocycles in the phthalocyanine molecules. There are, however, two methods of achieving solubility in almost all solvents. The first involves the use of a tri- or tetravalent transition metal as the core of the macrocycle, with the coordination compound having an axial ligand at the central metal.[3] The second method involves the introduction of various peripheral substituents on the macrocycle.[4] This minimizes the formation of aggregates, thereby improving the solubility.[5]

We have been studied the syntheses of functional dye materials based on 2,3-dicyanopyrazine chromophores, and correlated their physical properties with structures.[6] In this paper, we designed and synthesized metal and metal-free tetrapyrazinoporphyrazines derived from 2,3-dicyano-5-(4-*tert*-butylphenyl)-6-alkyl pyrazines derivatives for increasing solubility.

Treatment of these 4-(*tert*-butyl)alkyl phenone derivatives[7] with one equivalent of bromine in chloroform at room temperature gave α-brominated 4-(*tert*-butyl)alkyl phenone derivatives. α-Acetoxylated 4-(*tert*-butyl)alkyl phenone (obtained by the treatment of the α-brominated ketone with an excess of anhydrous potassium acetate in acetone) was reacted with 10% methanolic NaOH under reflux conditions to produce the corresponding compounds (**2**). The α-diketones (**3**) were obtained by the oxidation of α-hydroxyketone with copper sulfate in aqueous pyridine solution. Tetrapyrazinoporphyrazine precursors (**4**) were synthesized from α-diketones and diaminomaleonitrile, in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol.

The final tetrapyrazinoporphyrazine magnesium complexes (**5**) were successfully synthesized using excess magnesium butoxide in *n*-butanol under reflux conditions.[6] These magnesium complexes were easily demetalated. This was done by stirring them in excess *p*-toluenesulfonic acid, in THF, at room temperature, for 30 min, to produce **6** (in a yield range of 44-50%).[9] The reaction route is summarized



Scheme 1. Synthesis of tetrapyrazinoporphyrazine derivatives.

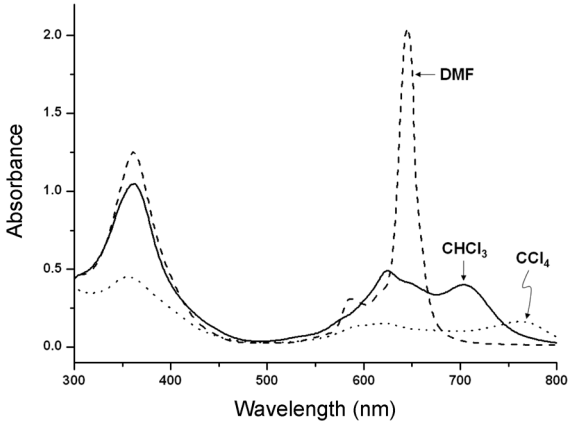


Figure 1. The effects of solvent polarities on the absorption spectra of **5a** (2.52×10^{-5} M).

in Scheme 1.

The absorption maxima in the electronic spectra of **5** and **6** in chloroform appeared at 625-705 nm, due to a π-π^* transition, commonly referred to as the Q-band. The small broadness around Q band region of **5** was generally observed because of structural mixtures resulting from their unsymmetrical structure. But the strange absorption curve observed in chlorinated solvent should be attributed to the molecular aggregation in solution (Figure 1).

Tetrapyrazinoporphyrazinato magnesium complexes (**5**) in *N*,*N*-dimethylformamide (DMF) showed red fluorescence with small Stokes shift values. The fluorescence of **5a** was greatly influenced by molecular aggregation. The Q-band spectrum causing the first π-π^* transition of **5** in DMF showed a pattern characteristic of a monomeric species, with a fluorescence maxima observed at 653-658 nm, as shown in Figure 1. On the other hand, **5a** in chloroform did not show any fluorescence and had patterns characteristic of an aggregate, as shown in Figure 2.

The Q-band spectra of **6** in chloroform and carbon tetrachloride showed patterns characteristic for a monomeric species with strong red fluorescence. However, the absorption spectra of **6** in DMF did not show split Q_x/Q_y bands. This is due to the electronic coupling between a pair (or more) of porphyrazine units.[10]

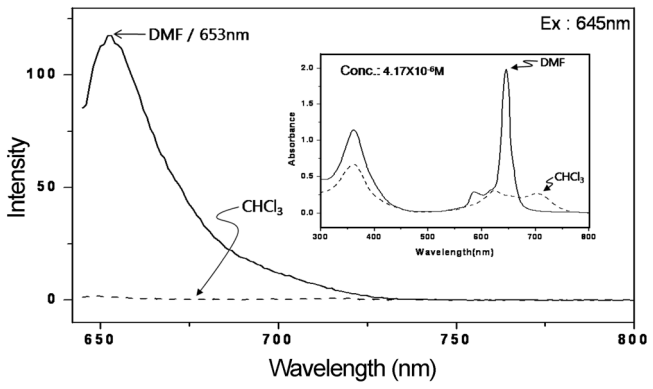


Figure 2. Emission spectra of **5a** (4.17×10^{-6} M) in DMF and $CHCl_3$.

In summary, we successfully synthesized organic-soluble tetrapyrazinoporphyrazines bearing long alkyl and *tert*-butyl phenyl substituents at peripheral positions. Porphyrazines **5** and **6** have satisfactory solubility in chlorinated hydrocarbons, THF, toluene, and *n*-hexane, but are practically insoluble in alcohols. Molecular aggregations and their functionalities will be reported elsewhere.

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8. *Typical procedure to synthesize **5a***: A suspension of Mg turnings (2 g, 0.08 mol), one small crystal of iodine, and *n*-butanol (150 mL) was heated under reflux for 4 h. The reaction mixture was then cooled to room temperature, and dicyanopyrazine **4a** (5.9 g, 0.02 mol) was added (all at once). The reaction mixture was quickly reheated to reflux. After approximately 10 min, the reaction mixture had become a dark green. After 1 h, the mixture was quenched by adding methanol (200 mL), and filtered, yielding the crude product as a dark green solid. The crude product was purified by column chromatography, using silica gel as the stationary phase, and chloroform/methanol (30/1) as the eluent. **5a** (dark green solid, 24%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 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); Anal. calcd. For $C_{72}H_{72}MgN_{16}$: C, 72.93; H, 6.12; N, 18.90. Found: C, 73.07; H, 6.05; N, 18.74; MALDI-TOF mass-spectra: m/z 1186.96 (calcd. 1185.75).
9. *Typical procedure to synthesize **6a***: *p*-Toluenesulfonic acid (27.5 g, 0.16 mol) was added to a solution of the Mg tetrapyrazinoporphyrazine (**5a**) (3.7 g, 3.1 mmol) in tetrahydrofuran (THF, 100 mL), and the resulting mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*, yielding the crude product as a dark green solid. The crude product was purified by column chromatography, using silica gel as the stationary phase, and chloroform/methanol (30/1) as the eluent. **6a** (dark green solid, 50%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ: −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); 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; MALDI-TOF mass-spectra: m/z 1164.84 (calcd. 1163.47).
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