

meso-Porphyrin의 합성과 분광특성

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Synthesis and Spectral properties of meso-porphyrin

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1. Introduction

The basic structure of porphyrin consists of four pyrrole units linked by four methine bridges. It reveals that the cyclic 16-atom is the preferred cyclic system for π -electron delocalization since this pathway exhibits the highest degree of bond equalization. Scheme 1 (a) shows the 16-center system is the chromogen of the porphyrins, which allows 18-electron delocalization that could produce aromatic characteristics [1,2]. Porphyrins and related tetrapyrrolic pigments occur widely in nature, and they play very important roles in various biological processes. Scheme 1 (b) and (c) shows the structures of major important porphyrins. 'Heme' is the prosthetic group in hemoglobins and myoglobins, which are responsible for oxygen transport and storage in living tissues. 'Heme' can also be found in the enzyme peroxidase, which catalyzes the oxidation of substrates with hydrogen peroxide. Certain Heme-containing proteins serve as one-electron carriers in the electron transport chain. Reduction of one of the pyrrole units on the porphyrin ring leads to a class of porphyrin derivatives called 'Chlorins' which found abundantly in green plants, belong to this category [3].

A large number of porphyrin derivatives have been synthesized for the purpose of molecular recognition [4-6]. Recently, the combination of porphyrins with another large organic molecule has always been an interesting route to new materials [7,8]. In this study, pyrazine-linked porphyrins were synthesized and their spectral properties were investigated.

2. Experimental

2.1. Synthesis of intermediate

To a suspension of 8.4 g (10 mmol) 2,3-bis(triphenylphosphonium methyl)-5,6-dicyanopyrazine dibromide (3) and 5 mmol of alkoxybenzaldehyde (5), which was prepared by the Williamson reaction of

benzaldehyde with corresponding alkylbromide, in ethanol (30 ml) at room temperature was added 1.8 g (25 mmol) sodium ethoxide (96%). The reaction mixture was refluxed for 4hr. After the reaction was complete, the reaction mixture was cooled. 5 mmol of terephthalaldehyde (4) was added, and then reaction mixture was heated for reflux condition. The reaction mixture was cooled to room temperature.

The precipitate was filtered. The crude product was purified by column chromatography.

2.2. Synthesis of *meso*-porphyrins

A solution of compound 6 (2 mmol) and pyrrole (2 mmol) in chloroform (100ml) was purged with nitrogen for 10 min, BF₃ (0.5 mmol) was added. The solution was stirred for 1 hr at room temperature. Then 2 mmol of 2,3-dichloro-4,5-dicyanoquinone (DDQ) was added and the mixture was stirred over night. The solvent was removed and the residue was triturated with chloroform. The solution was washed with 1M aqueous sodium carbonate solution, water, brine, and dried over Na₂SO₄. After the solvent was removed, the crude product was purified by column chromatography.

3. Results and Discussions

3.1. Synthesis

Treatment of 1,4-dibromobutane-2,3-dione (1) and diamino- maleonitrile (DAMN) in the presence of catalytic amount of *p*-toluenesulfonic acid in ethanol under reflux condition afford the 2,3-bis(bromomethyl)-5,6-dicyanopyrazine (2). The reaction of 2 with 2,3-bis (triphenyl phosphoniummethyl)-5,6-dicyanopyrazine dibromide (3) in the two equivalent of triphenylphosphine in toluene afforded in good yield (78%). 4-Alkoxybenzaldehyde (5) was synthesized by the reaction of 4-hydroxybenzaldehyde and various alkylbromide in the presence of excess potassium carbonate in acetone in good yield (>90%). Reaction of 3 with one equivalent of terephthalaldehyde (4) in the presence of two equivalent of sodium ethoxide under reflux conditions gave the styryl intermediate. And then the various alkoxybenzaldehyde (5) was added in the reaction mixture to give 2,3-dicyanopyraine compound 6. Reaction pathways are summarized in scheme 2.

The ¹H NMR spectrum of 6 indicated that ethylene protons appeared doublets at 7.43 ppm (*J* = 15.6 Hz) and 7.82 ppm (*J* = 15.3 Hz). According to coupling constant, compound 6 should exist in *trans*-configuration.

5,10,15,20-tetra[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (8) was prepared by condensation reaction of pyrrole and 2,3-dicyanopyrazine intermediate (6) in moderate yield (15-27 %). The chemical structures was identified by FT-IR, ¹H NMR spectroscopy.

The aromatic character of porphyrins can also be seen by ¹H NMR spectroscopy. Due to the anisotropic effect from the porphyrin ring current, the NMR signals for the deshielded -protons show up at low field (8 to 9 ppm), whereas the signals for the shielded protons on the inner nitrogen atoms show up at high field (-2.8 ppm).

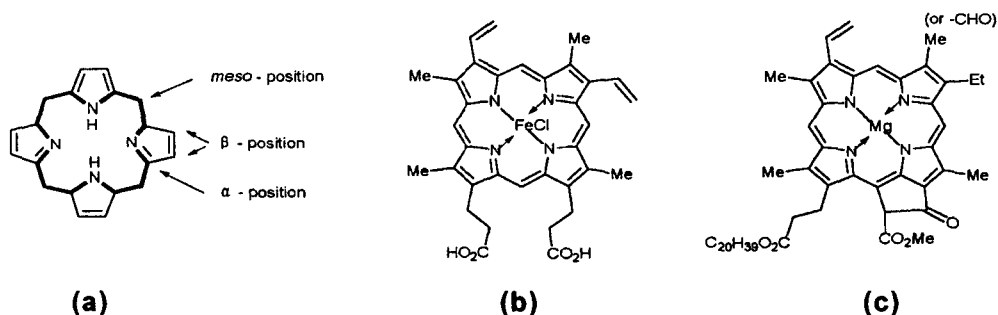
3.2. Spectral properties

Figure 1 shows the visible and fluorescence spectra of intermediate compound 6. Two absorption peaks were observed at 340 and 412 nm in chloroform. The absorption band at around 412 nm was resulted from the π - π^* transition due to the strong electron withdrawing cyano group. The fluorescence maximum was observed at 532 nm excited at 412 nm. The stoke's shift value was 120nm, which indicated the energy loss in the excited state. This may be observed when a molecule in the first excited state adopts a more coplanar configuration than in the ground state.

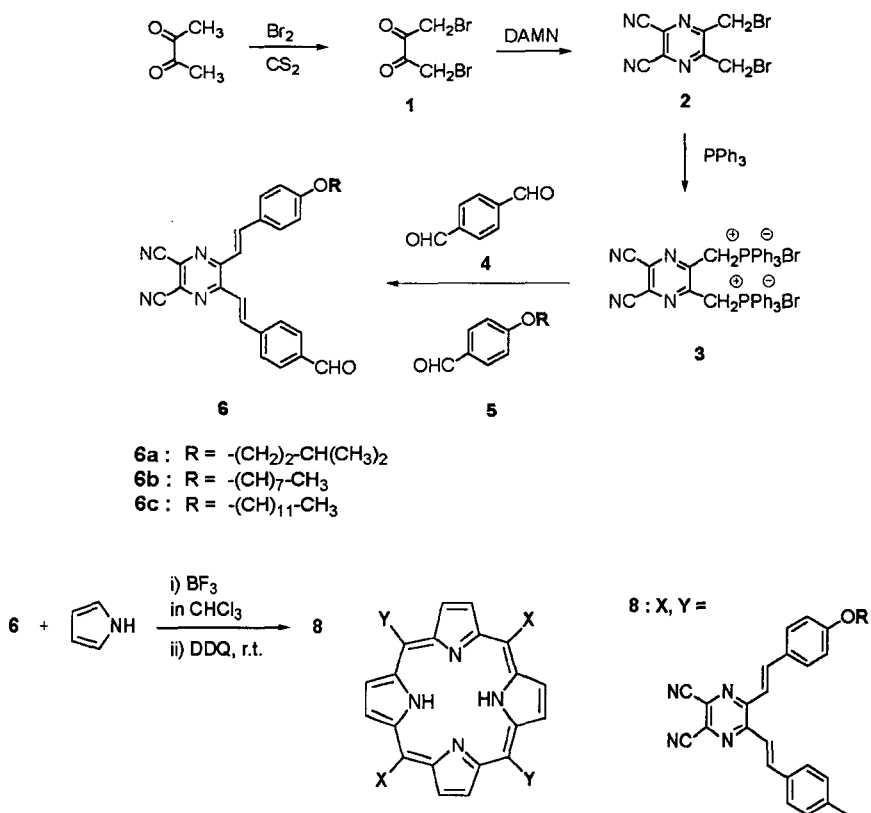
All porphyrins have strong fluorescence at around 536 nm. These results is interested in the porphyrin application. These fluorescent compounds have good thermal and chemical stability compared to those of monomeric organic materials.

4. References

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Scheme 1. Chemical structures of natural porphyrins.



Scheme 2. Reaction route of porphyrins.

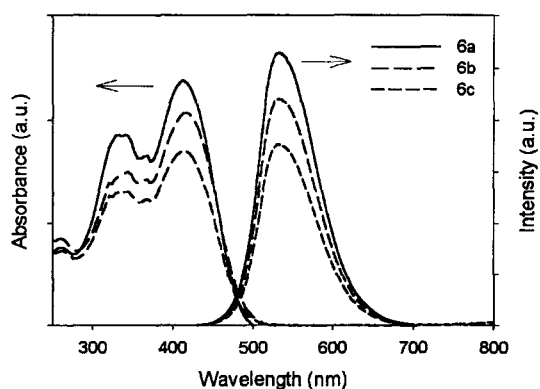


Figure 1. The UV-visible and fluorescent spectra of intermediate (6) in chloroform.