Synthesis and Characterization of *meso*-Substituted Porphyrins Bearing 2,3-Dicyanopyraiznes

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The basic structure of porphyrin consists of four pyrrole units linked by four methine bridges. This indicates that the cyclic 16-atom is the preferred cyclic system for π-electron delocalization since this pathway exhibits the highest degree of bond equalization. Porphyrins and related tetrapyrrolic pigments occur widely in nature, and they play very important roles in various biological processes. A large number of porphyrin derivatives have been synthesized for the purpose of molecular recognition.[1-3] There are two general approaches to obtain a desired porphyrin: modification of natural porphyrins and total synthesis. Although convenient, modification of naturally occurring porphyrins poses great limitations on the choice of peripheral substituents because certain substituents cannot be modified easily. In most cases, such limitations can be overcome by total synthesis, which involves the synthesis of the pyrrole having the required substituents. As mentioned above, the size and symmetry of monomeric structures can be relatively easily controlled.[4-6]

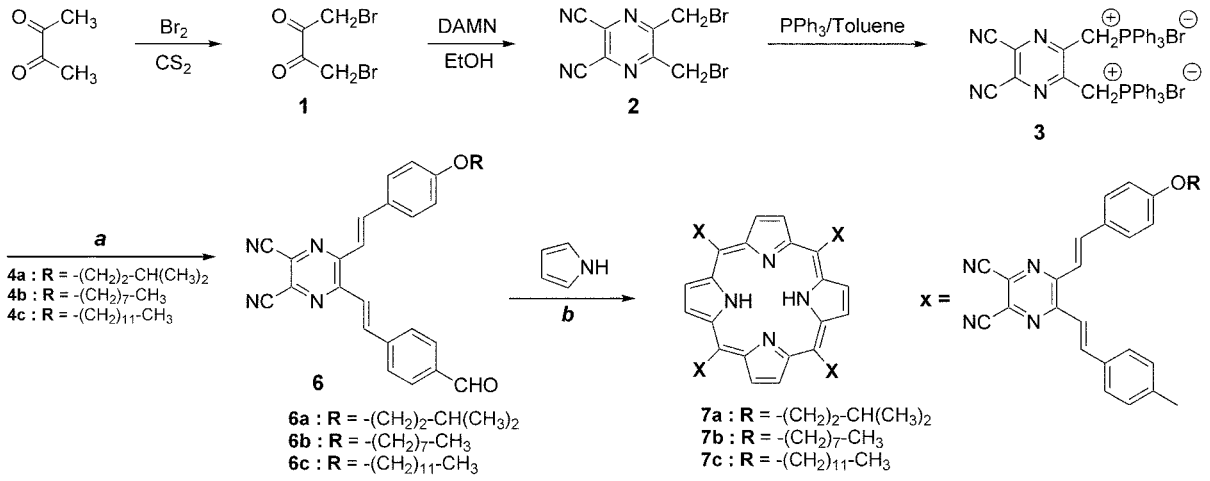
Among the great diversity of porphyrins with a specific pattern of substituents, *meso*-substituted porphyrins have recently received great attention. The most popular method for the synthesis of *meso*-substituted porphyrins is by the reaction of dipyrrolmethanes with aldehydes.[7] These compounds have been useful materials in many fields such as energy transfer material (solar cell), biomedical, chemical sensor, and photodynamic therapy.[8-13]

Recently, the combination of porphyrins with another large organic molecule has become an interesting route to new materials.[14,15] In this study, pyrazine-linked porphyrins were synthesized and their characteristics were investigated.

Treatment of 1,4-dibromobutane-2,3-dione (**1**) and diaminomaleonitrile (DAMN) in the presence of a catalytic amount of *p*-toluenesulfonic acid in ethanol under reflux condition afforded 2,3-bis(bromomethyl)-5,6-dicyanopyrazine (**2**). The reaction of compound **2** with two equivalents of triphenylphosphine in toluene afforded 2,3-bis(triphenylphosphoniummethyl)-5,6-dicyanopyrazine dibromide (**3**) at a good yield of 78%.[16] 4-Alkoxybenzaldehyde (**4**) was synthesized by the reaction of 4-hydroxybenzaldehyde and various alkylbromides in the presence of excess potassium carbonate in acetone at high yields of more than 90%.

Reaction of compound **3** with one equivalent of 4-alkoxybenzaldehyde (**4**) in the presence of two equivalents of sodium ethoxide gave the mono-styryl intermediate. The excess of terephthalaldehyde (**5**) was added in the reaction mixture to give 2,3-dicynopyrazine (**6**). The ^{1}H NMR spectrum of compound **6** indicated that ethylene protons appeared as doublets at 7.43 ppm (J = 15.6 Hz) and 7.82 ppm (J = 15.3 Hz). According to the coupling constant, compound **6** should exist in *trans*-configuration.

The compound 5,10,15,20-tetra[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**7**) was prepared by condensation reaction of pyrrole and



Scheme 1. *Reagents and conditions*: (a) i) 1.0 equiv. 4-Alkoxybenzaldehyde (**4**)/2.0 equiv. EtONa, EtOH/DMF (13 : 10), 80 °C, 4 h ; ii) 2.0 equiv. Terephthalaldehyde (**5**), 100 °C, 3 h; (b) i) 0.25 equiv. BF_3, $CHCl_3$, rt, 1 h; ii) 1.0 equiv. DDQ, rt, overnight.

bis-styryl derivative (**6**) containing dicyanopyrazine at a moderate yield of 15-27%.

The porphyrazine ring can act both as an acid and a base. Strong bases can remove the two protons on the inner nitrogen atoms of a porphyrin to form a dianion. On the other hand, the two free pyrrolic nitrogen atoms can be protonated easily with acids.

When a trace amount of acid was added to the free base porphyrazine solutions, typical protonation of the inner nitrogen in the porphyrazine rings was observed in all cases. The typical absorption change of porphyrazine with increasing concentration of the acid is shown in Figure 1. As the amount of *p*-toluenesulfonic acid (p-TSA) increased in porphyrazine **7c** solution, the characteristic Soret bands at 444 nm were shifted to 480 nm, while the Q band at 694 nm was moved to 688 nm. Simultaneous isosbestic points indicated the presence of an acid/base equilibrium process. Porphyrazines (**7c**) can undergo deprotonation reaction by the addition of sodium ethoxide (Figure 2). The deprotonation reaction leads to a decreased Q band at around 690 nm.

The effects of pH on porphyrazine spectral changes can generally be explained by partial charge transfer from the nitrogen atom to the porphyrazine π-electron system under

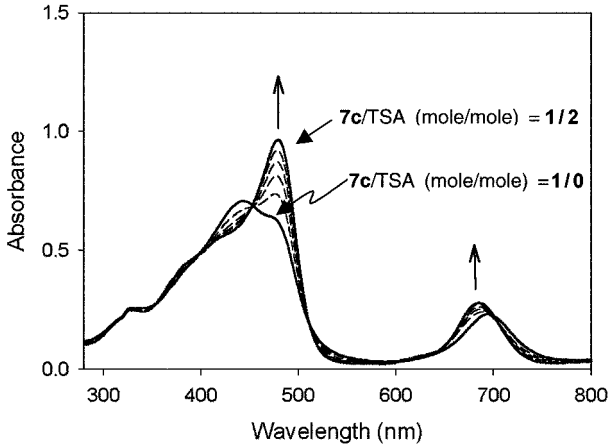


Figure 1. Spectral change of **7c** in chloroform (2×10^{-6} M) as increasing of *p*-toluenesulfonic acid (TSA).

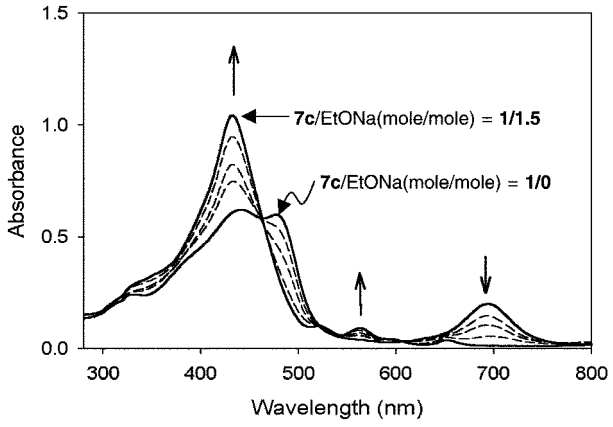


Figure 2. Spectral change of **7c** in chloroform (2×10^{-6} M) as increasing of sodium ethoxide.

the formation of stabilized cation, which can be represented in different resonance structures. It is well known that porphyrazines are likely to exist in solution as nonequivalent tautomers (as indicated by the 22π electron delocalization pathways highlighted in bold for the structures).

In summary, the pyrazine-linked porphyrins were synthesized and their characteristic was investigated. The typical absorption change of porphyrazine **7** with increasing concentration of the acid was observed. Simultaneous isosbestic points indicated the presence of an acid/base equilibrium process.

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17. Typical procedure to synthesize 5,10,15,20-tetra[5-{2-(4-amyloxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**7a**); A solution of compound **6** and equimolar amount of pyrrole in chloroform was purged with nitrogen for 10 min, 0.25 equivalent of $BF_3 \cdot OEt_2$ was added. The solution was stirred for 1 hr at room temperature. Then 1 equivalent of 2,3-dichloro-4,5-dicyanoquinone (DDQ) was added and the mixture was stirred overnight. The solvent was removed and the residue was triturated with chloroform. The solution was washed with 1 M aqueous sodium carbonate solution, water, brine, and dried over Na_2SO_4. After the solvent was removed, the crude product was purified by column chromatography in silica gel, eluting with chloroform; 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (m, 8H), 8.36-8.34 (m, 12H), 8.08-7.98 (m, 12H), 7.60-7.57 (m, 12H), 6.95-6.92 (m, 12H) 4.01 (t, 8H, Ar-O-**CH$_2$**), 1.88-1.80 (m, 4H, >**CH**-(CH$_3$)$_2$), 1.79-1.65 (m, 8H, methylene), 0.98 (d, 24H, >CH-(**CH$_3$**)$_2$), -2.78 (s, 2H). Calcd. for $C_{128}H_{102}N_{20}O_4$: C, 77.48; H, 5.18; N, 14.12; Found. C, 77.12; H, 4.85; N, 13.78.