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Short communication

The synthesis and optical properties of *meso*-substituted porphyrins bearing quinoxaline derivatives

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Abstract

Porphyrins bearing quinoxaline derivatives were synthesized by the condensation reaction of 2,2′-(*p*-tolylmethylene)bis(1*H*-pyrrole) and a bisstyryl derivative containing 6,7-diisopentyloxyquinoxaline. The highly conjugated porphyrin macrocycle showed intense absorption at ∼425 nm (Soret band), followed by several weaker absorptions (Q band) at higher wavelengths (680 nm). The porphyrins showed strong fluorescence at ∼480 nm. The chromophoric system of the fluorescent and highly conjugated porphyrin macrocycles were studied from the viewpoint of protonation and deprotonation effects on their absorption and emission spectra in solution.

Keywords: *meso*-Porphyrin; Absorption spectra; Q band; Spectral change

1. Introduction

The basic structure of porphyrins consists of four pyrrole units linked by four methine bridges. This indicates that the cyclic 16-atom structure 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 play very important roles in various biological processes. A large number of porphyrin derivatives have been synthesized for the purpose of molecular recognition [1,2].

Among the great diversity of porphyrins with a specific pattern of substituents, *meso*-substituted porphyrins have recently received a great deal of attention. The most popular method of synthesizing *meso*-substituted porphyrins is by the reaction of dipyrromethanes with aldehydes [3]. These compounds have been found to be useful materials in many fields such as energy transfer (solar cells), biomedical, chemical sensors, and photodynamic therapy [4–9]. Recently, the combination of porphyrins with another large organic molecule has become an interesting route to new materials [10,11].

In case of porphyrin complexes, protonation/deprotonation of the macrocycle is generally not considered, unless dissociation of the central atom occurs. However, for some complexes of *meso*-substituted octaalkylporphyrines, the possibility of protonation of the macrocycle and formation of carbocations was also demonstrated [12].

In this study, quinoxaline-linked porphyrins were synthesized and the effects of protonation and deprotonation on their absorption and emission spectra in solution were investigated.

2. Results and discussion

2.1. Synthesis

Quinoxaline derivatives (**1**–**3**) and 2,2′-(*p*-tolylmethylene)-bis(1*H*-pyrrole) (**5**) were synthesized by the method described in the literature [13–16]. The reaction of compound **3** with 1 equiv of *p*-tolualdehyde in the presence of 2 equiv of potassium *tert*-butoxide gave the mono styryl intermediate. This crude product was used in the next step without purification.

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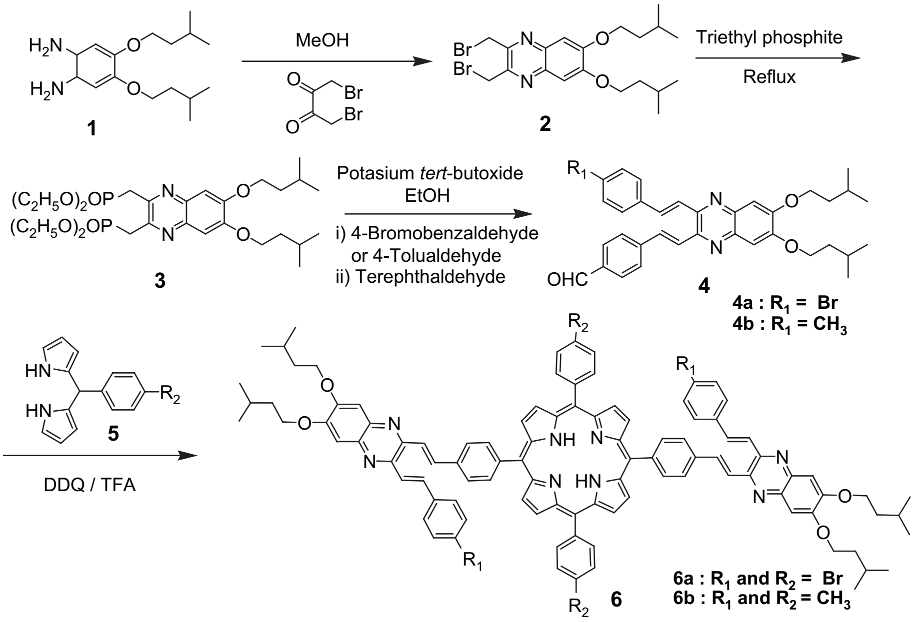

Scheme 1. Synthetic route of *meso*-porphyrins linked quinoxaline.

An excess amount of terephthaldehyde was added to the reaction mixture to give (*E*)-4-(2-(6,7-bis(isopentyloxy)-3-(4-methylstyryl)quinoxalin-2-yl)ethyl)benzaldehyde (**4b**) [17]. The crude product was purified by column chromatography (silicagel, ethyl acetate/*n*-hexane = 5:1).

The *meso*-substituted porphyrin-linked quinoxaline derivative (**6b**) was prepared by the condensation reaction of 2,2′-(*p*-tolylmethylene)bis(1*H*-pyrrole) (**5b**) and compound **4b** in the presence of trifluoroacetic acid (CF_3COOH) in chloroform. The crude product was purified by column chromatography (silicagel, ethyl acetate/*n*-hexane = 1:3) [18].

In the ^{1}H NMR spectrum of compound **6** in $CDCl_3$, due to the anisotropic effect resulting from the porphyrin ring current, the NMR signals for the deshielded β-protons show up at low field (8.9 ppm), whereas the signals for the shielded protons on the inner nitrogen atoms show up at high field (−2.6 ppm). In the aliphatic region, a sharp triplet resonance corresponding to O-methylene protons ($O-CH_2$) at 4.23 ppm was observed. The reaction pathways involved are summarized in Scheme 1.

2.2. Optical properties (absorption and emission spectra)

The typical UV−vis spectra of the neutral *meso*-substituted porphyrin-linked quinoxaline derivative (**6**) exhibited characteristic Soret and Q bands. The Q band observed at 680 nm in the visible region was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the porphyrin ring, while the Soret band observed at 425 nm was ascribed to the deeper π-level → LUMO transition.

The porphyrin ring can act as both 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 easily be protonated with acids.

The halochromism properties of *meso*-tetrakis(*p*-methoxy phenyl)porphyrin(*p*-$OMeTPPH_2$) have been evaluated by Manna and co-workers [19]. The Q-band maximum for the free base form, the protonated form and the deprotonated form of *p*-$OMeTPPH_2$ were reported to be appeared at 626 nm, 650 nm and 692 nm, respectively. However, the quinoxaline-linked porphyrins **6** show the different halochromism behavior compared to that of *p*-$OMeTPPH_2$.

When a trace amount of acid was added to the free base porphyrin (**6**) solutions, a typical protonation of the inner nitrogen in the porphyrin rings was observed in all cases. The typical change in the absorption spectra of the porphyrin

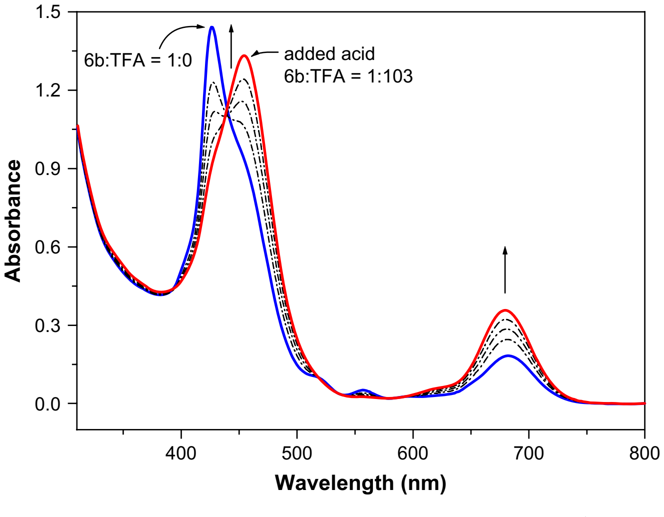

Fig. 1. Absorption spectra changes of **6b** in $CHCl_3(1.936 \times 10^{-5}$ M) with increasing concentration of trifluoroacetic acid.

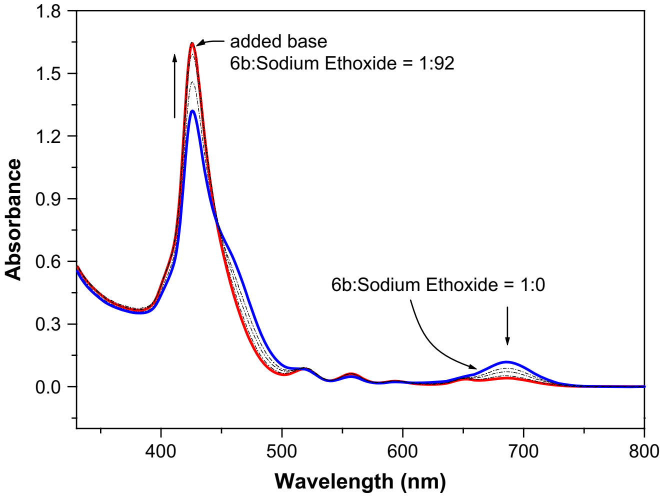

Fig. 2. Absorption spectra changes of **6b** in $CHCl_3$(1.936×10^{-5} M) with increasing concentration of sodium ethoxide.

with increasing concentration of acid is shown in Fig. 1. As the amount of trifluoroacetic acid in the solution of porphyrin **6b** was increased, the characteristic Soret bands at 426 nm were shifted to 455 nm, while the intensity of the Q band at around 680 nm increased. The existence of an isosbestic point indicated the presence of an acid/base equilibrium process. Porphyrin **6b** undergoes a deprotonation reaction upon the addition of sodium ethoxide (Fig. 2). This deprotonation reaction leads to a decrease in the intensity of the Q band at around 680 nm.

The typical changes in the emission spectra of porphyrin **6b** caused by the addition of an acid or base are shown in Fig. 3. In contrast to the fluorescence of **6b** in $CHCl_3$/MeOH (9:1) solution, the gradual addition of sodium ethoxide to a $CHCl_3$/MeOH (9:1) solution of **6b** leads to a continuous decrease in the intensity of the fluorescence maximum (482 nm). However, a new fluorescence maximum at 564 nm was observed when acid (CF_3COOH) was added to a $CHCl_3$/MeOH (9:1) solution of **6b**.

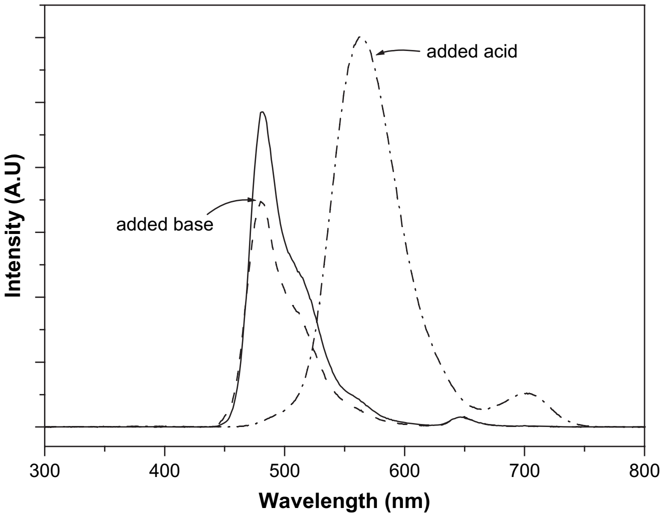

Fig. 3. Emission spectra changes of **6b** in $CHCl_3$ (3.4×10^{-5} M) at acid and base conditions.

The effects of pH on the spectra of these porphyrins can be explained by the partial charge transfer which occurs from the nitrogen atom to the porphyrin π-electron system through the formation of a stabilized ion, which can be represented by different resonance structures.

3. Conclusions

Several porphyrins bearing quinoxaline derivatives containing substituents with different electron donating ability were synthesized. The existence of an isosbestic point in the spectrum of each derivative indicated the presence of an acid/base equilibrium process.

Acknowledgements

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[17] **4b**: 40% yield, m.p.: 157–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 ppm (d, 12H, CH_3), 1.82–1.86 ppm (m, 6H, CH and CH_2), 2.40 ppm (s, 3H, Ar–CH_3), 4.22 ppm (t, 4H, OCH_2), 7.22 ppm (s, 2H, quinoxaline ring), 7.56–7.89 ppm (m, 12H, aromatic proton and vinyl), 9.96 ppm (s, 1H, Ar–CHO). Calculated for $C_{36}H_{40}N_2O_3$: C, 78.80; H, 7.35; N, 5.11; found: C, 78.10; H, 7.01; N, 4.93.

[18] General procedure: a solution of **4b** (2 mmol) and 2,2′-(*p*-tolylmethylene)bis(1*H*-pyrrole) (**5b**) (2 mmol) in 50 ml $CHCl_3$ was purged with argon for 10 min, then CF_3COOH (260 μL of 2.5 M stock solution in $CHCl_3$, 26 mM) was added. The solution was stirred for 1 h at room temperature then DDQ (1.5 mmol) was added. The mixture was stirred at room temperature for an additional 1 h and then the solvent was removed. The crude product was purified by column chromatography (silicagel, ethyl acetate/*n*-hexane = 1:3). **6b**: 5% yield, m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ −2.54 (s, 2H, pyrrole), 1.04 (s, 24H, CH_3), 1.80–1.92 (m, 12H, CH_2CH), 2.41 (s, 6H, Ar–CH_3), 2.71 (s, 6H, Ar–CH_3), 4.23–4.28 (t, 8H, OCH_2), 7.23–8.92 (m, 44H); MALDI-TOF-mass-spectra: *m*/*z* 1528.5839 (100%, calcd. 1527.97). Calculated for $C_{104}H_{102}N_8O_4$: C, 81.75; H, 6.73; N, 7.33; found: C, 81.21; H, 6.35; N, 7.02.

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