Unusual Absorption Spectra Found for Some Phthalocyaninatozinc(II) Complexes Bearing Dendritic Substituents at α Positions

Kuninobu Kasuga,* Noriyuki Matsuura, Koji Inoue, Makoto Handa, Tamotsu Sugimori, Kimio Isa,[†] and Makoto Nakata[††]
Department of Material Science, Faculty of Science and Engineering, Shimane University, Nishikawatsu, Matsue 690-8504
[†]*Department of Natural Science, Faculty of Education, Fukui University, Fukui 910-8507*
[††]*Peptide Institute, 4-1-2 Ine, Shinonome 562-8686*

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Phthalocyaninatozinc(II) complexes bearing dendritic substituents have been prepared. It was found that their generation number and positions on the phthalocyanine ring caused unusual absorption and emission spectral features.

Metalloporphyrins encapsulated into the interior core of dendrimer (Den) have received much attention from the viewpoints of their photophysical and electrochemical properties, oxygen-binding nature, regioselective catalytic activity, and energy transfer ability.[1]

Recently, Den-substituted derivatives of phthalocyanines and their metal complexes (Mpcs) were also prepared and reported on their prominent nature such as avoiding aggregation or forming glass as well as interesting photophysical properties.[2–6]

Since Mpcs intensively absorb the longer wavelength of visible light in the solar spectrum, they are attractive sensitizers for photoreduction of water, carbon dioxide or ethylene.[7,8] Den-substituted Zn(II)pcs are then expected as potential sensitizers for the regio- and shape-selective photooxidation.[9,10]

The Den substituents in Mpcs reported previously were all introduced at β positions on the pc ring (α and β shown in Figure 1 denote the substituted positions on the pc ring). To elucidate the effect of the Den position of the pc ring on the steric crowdedness around the ring, the phthalocyaninatozinc(II) complexes substituted by Dens at the α or β position of the pc ring, Znpc{α (or β)-G$_n$} (the subscript n denotes a number of its generation as shown in Figure 1) were prepared. We here report Znpc(α-G$_n$) complexes showing unusual abosprtion spectra in nonpolar solvents.

3(or 4)-Den-substituted phthalonitriles were prepared by stirring a *N*,*N*-dimethylformamide (DMF) solution of 3(or 4)-nitrophthalonitrile and corresponding Den-OH in the presence of potassium carbonate at room temperature for a few days.[11,12] The 1-octanol solution of phthalonitrile derivatives and a small amount of metal lithium was heated at *ca.* 80 °C for 30 min. Into the dark green solution, was a small amount of DMF–*N*-ethyldiisopropylamine solution (1 : 1, v/v %) containing zinc(II) chloride added, the reactant being further heated for 1 h at *ca.* 80 °C. The obtained crude phthalocyanine derivatives were twice purified by silica gel column chromatography. The green powders were obtained by recrystallization from chloroform and hexane mixed solvent.[13]

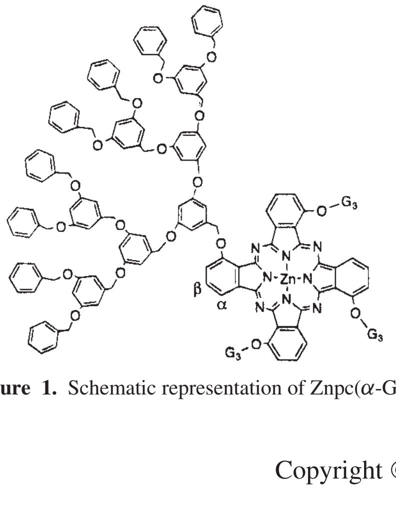

Figure 1. Schematic representation of Znpc(α-G$_3$).

Znpc(α-G$_3$) showed Q$_{0\text{-}0}$ and Soret bands of the pc ring as well as a π-π^* transition band of the dendritic substituent at 705, 322, and 282 nm in dichloromethane, and Znpc(β-G$_3$) showed those bands at 683, 337, and 279 nm, respectively. The Q bands of the α-substituted complexes are more red-shifted compared with those of the β-substituted ones, which means that the bands are dependent on the substituted position on the pc ring.[14] The α-substituted complexes also showed new bands (named as X bands) at the longer wavelength side of the Q band (723$^{\mathrm{sh}}$, 759 nm), of which intensities increased with decreasing that of the Q band by standing the solution at room temperature (Figure 2). The spectral change was further accelerated by warming the solution. The X bands were also observed in chloroform and benzene, but did not appear in polar solvents, DMF, dimethyl sulfoxide, and acetone. On the other hand, the β-substituted complexes did not show the X bands even in the nonpolar solvents.

Appearance of the X bands was most remarkable in the case of Znpc(α-G$_3$); after standing the solution for a day, the bands with relatively strong intensity were observed and the original

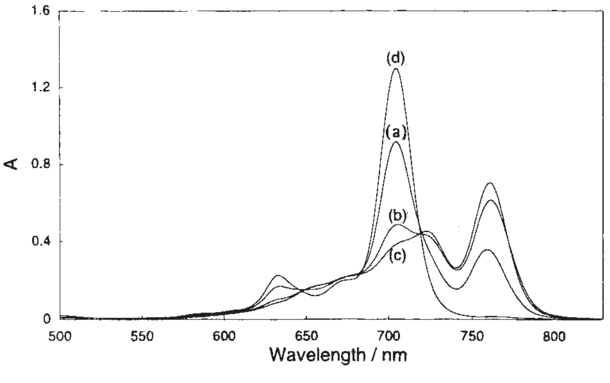

Figure 2. Electronic absorption spectral changes of the dichloromethane solution containing Znpc(α-G$_3$) at room temperature. [complex] = 1.2×10^{-5} mol dm^{-3}. (a) just after being dissolved, (b) after 12 h, (c) after 24 h, (d) after adding a drop of pyridine to the (c) solution.

spectrum was immediately recovered by adding a small amount of pyridine to the solution (Figure 2). In the case of Znpc(α-G_1) and Znpc(α-G_2), the X bands also appeared, but their intensities were weak compared with that of Znpc(α-G_3).

In order to investigate the origin of the X bands, fluorescence spectra were measured; we designate the species with the Q band at 705 nm and that with the X bands at 723^{sh} and 759 nm as A and B species, respectively. Both the species showed fluorescence when they were excited at their Soret bands. The S_1 emission of the B species (773 nm) was more red-shifted compared with that of the A species (712 nm), and the former intensity was weaker than the latter one due to the fact that the decrease of the energy gap between excited and ground states results in the increase of a nonradiative transition from the excited state to the ground one (ϕ_F for the A and B species are 0.37 and 0.16, respectively).[15] The emission spectral results support the presence of two kinds of species in solution. Both the species also showed the S_2 emission around 450 nm (ϕ_F for the A and B species are 0.004 and 0.003, respectively), of which values were in the same range as those of usual Mpcs.[16–18]

It is known that the Q bands of Mpcs are shifted to the longer wavelength region by formation of the slipped face-to-face dimer.[19,20] Furthermore, the red shift of the Q bands were reported for the zeolite encapsulated Mpcs, of which pc rings are considered to be distorted so as to reside in the narrow cavities of the zeolite.[21] It is also reported that peripherally crowded porphyrin complexes, of which rings are severely distorted, leading to the red shift of the Soret bands.[22–24] Recently, Kobayashi et al. reported that the ring of pcH_2 substituted with eight phenyl groups at the α-positions is tremendously distorted, showing the Q band at 788 nm.[25]

The relative intensity (I_B/I_A) of the band maxima at 705 nm (I_A) and 759 nm (I_B) slightly decreased with increasing the concentration of the complexes. This result ruled out the possibility of the slipped face-to-face dimer as the X bands origin because the increase in the concentration should increase the dimer formation. The oxidation of the pc ring gives rise to a new band at the longer wavelength side of the Q band. In this case, a relatively strong band should be accompanied in the wavelength range from 500 to 600 nm.[26] However, such the band was not observed for the present complex (Figure 2), which also excludes the posibility of the pc-ring oxidation as the X-bands origin.

It may be assumed that the oxygen atoms of Den can coordinate to the zinc(II) ion, which results in the pc-ring distortion and shifts the Q band to the longer wavelength, as shown in the case of the encapsulated Mpcs or the crowded porphyrin complexes. This could be related to the appearance of the X bands of the B species, which is supported by the fact that the addition of pyridine into the solution containing the B species decreased the intensity of the X bands due to the coordination of pyridine to the zinc(II) ion instead of the oxygen atoms of Den. Znpc(β-G_3) did not show the X bands. The oxygen atoms of Den intoroduced at the β positions are considered to be too far from the central zinc(II) ion to coordinate. On the contrary, Den introduced at the α positions can give the coordination of the oxygen atoms because they are close enough to coordinate to the central ion.

Although the detailed analysis based on the NMR data was considered important for the assignment of the X-bands origin, it was difficult because the amount of the B species with the X band decreased in solution when the concentration was increased for enhancing the quality of the NMR data. However, in consideration of the spectral results reported for the peripherally crowded porphyrin and pc complexes, it seems reasonable to suppose that the pc-ring distortion caused by the steric hindrance between the Den substituent and the pc-ring is related to the appearance of the X bands.

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13 Znpc(α-G_1): Yield 43%. ^{1}H NMR ($CDCl_3$): δ 4.65–5.09 (m, 16H), 5.40–5.68 (m, 8H), 6.35–6.54 (br m, 4H), 6.67–7.37 (br m, 48H), 7.54–8.90 (br m, 12H). Anal. Calcd for $C_{116}H_{90}N_8O_{12}Zn$: C, 75.26; H, 4.79; N, 6.05%. Found: C, 74.67; H, 5.01; N, 5.90%. MS (MALDI-TOF) m/z obsd 1852.77 ($[M + H]^+$), Calcd for $C_{116}H_{90}N_8O_{12}Zn$: 1851.38. Znpc(α-G_2): Yield 7.2%. ^{1}H NMR ($CDCl_3$): δ 4.64–5.09 (m, 48H), 5.52 (br s, 8H), 6.09–6.73 (m, 36H), 6.92–7.54 (m, 80H), 7.73–8.74 (br m, 12H). Anal. Calcd for $C_{228}H_{184}N_8O_{28}Zn$: C, 77.15; H, 5.23; N, 3.16%. Found: C, 77.53; H, 5.48; N, 2.58%. MS (MALDI-TOF) m/z obsd 3550.15 ($[M + H]^+$), Calcd for $C_{116}H_{90}N_8O_{12}Zn$: 3549.43. Znpc(α-G_3): Yield 7.5%. ^{1}H NMR ($CDCl_3$): δ 4.52–5.22 (br m, 76H), 5.33 (s, 8H), 6.26–6.66 (br m, 76H), 6.77 (br s, 8H), 7.06–7.41 (br m, 160H), 7.82–8.94 (br m, 12H). Anal. Calcd for $C_{452}H_{376}N_8O_{60}Zn$: C, 78.17; H, 5.46; N, 1.61%. Found: C, 78.32; H, 5.69; N, 1.26%. MS (MALDI-TOF) m/z obsd 6946.76 ($[M + H]^+$), Calcd for $C_{452}H_{376}N_8O_{60}Zn$: 6945.43. Znpc($\beta$-$G_3$): Yield 9.3%. Anal. Calcd for $C_{452}H_{376}N_8O_{60}Zn$: C, 78.17; H, 5.46; N, 1.61%. Found: C, 78.24; H, 5.81; N, 1.03%. MS (MALDI-TOF) m/z obsd 6945.92 ($[M + H]^+$), Calcd for $C_{452}H_{376}N_8O_{60}Zn$: 6945.43.

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