# Regiospecific and Nonlinear Substituent Effects on the Electronic and Fluorescence Spectra of Phthalocyanines

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The position and bandwidth of the Q band of phthalocyanines (Pcs) vary according to the kind of central metal and the type, number, and positions of peripheral substituent groups.[1] For example, the $Q_{0-0}$ bands of ZnPcs generally lie at longer wavelengths and have sharper bandwidths than those of CoPcs. Concerning the shift of the $Q_{0-0}$ band position by substituent groups, it is known that an approximate additivity exists when the same substituents are introduced at the same position of each benzene ring of the Pcs. A good example is seen in the case of *tert*-butylated ZnPcs.[2] In dimethyl sulfoxide, the $Q_{0-0}$ bands of (i) unsubstituted ZnPc, (ii) $2^2$-*tert*-butylbenzo[*b*]tribenzo[*g,l,q*]-5,10,15,20-tetraazaporphine, and (iii) $2^2,7^2,12^2,17^2$-tetra-*tert*-butylbenzo[*b,g,l,q*]-5,10,15,20-tetraazaporphyrin appear around 670 nm and the energy difference between (i) and (iii) (139 $cm^{-1}$) is approximately four times larger than that between (i) and (ii) (33 $cm^{-1}$). However, the effect of introduction of a plurality of substituent groups on each benzene unit has not been examined systematically to date. In this communication, we report regiospecific and nonlinear substituent effect of alkoxyl groups on the shift of the electronic and fluorescence spectra, on the quantum yields ($\Phi_F$) of fluorescence emission of metal-free and zinc Pcs, and on the splitting of the $Q_{0-0}$ band of metal-free Pcs.

The structures and abbreviations of the compounds used in this study are shown in Chart 1. They were prepared by the so-called "nitrile" or "isoindoline" method,[3] purified using basic alumina and subsequently gel-permeation columns (Bio-Beads SX-2 or -8), and recrystallized from appropriate solvents.[4] $H_2$-Pc alone was purified by sublimation.[4]

**Chart 1**

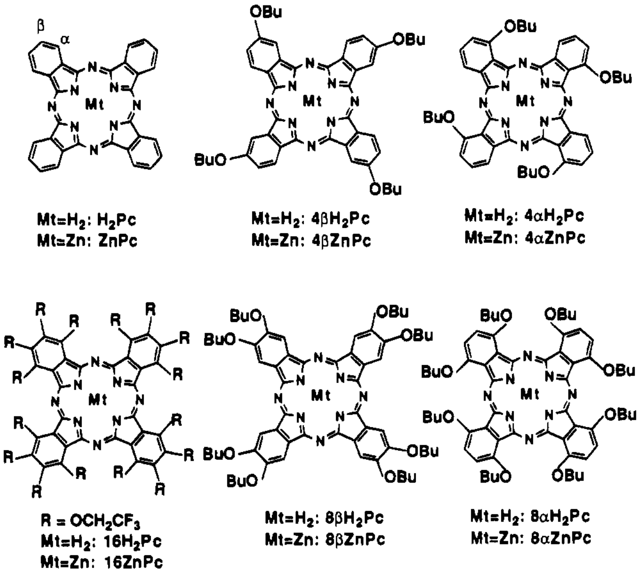

Figure 1 shows the electronic absorption spectra of six ZnPcs and the magnetic circular dichroism (MCD) of three representative ZnPcs in the Q band region. Although the spectra in the Soret region are not shown, generally both the Q and Soret bands shift to longer wavelengths with the attachment of alkoxyl groups. However, careful inspection reveals the following points. ( i) The effect of substituents at an α position is much larger than that at a *β* position (for α and *β* positions, see unsubstituted structure in Chart 1). (ii) Introduction of the second alkoxyl group at the *β* position shifts the Q band slightly to shorter wavelengths. (iii) Alkoxyl groups at α positions reduce the values of the absorption coefficients ($\epsilon$) of both the Soret and Q bands. (iv) In contrast to the higher energy shift of the Q band on introduction of the second alkoxyl group at the *β* position (above (ii)), the second alkoxyl group at the α position greatly shifts not only the Q but also the Soret bands to the red. In particular, as summarized in Table 1, the second alkoxyl group is *ca.* 1.5–1.8 times more effective than the first alkoxyl group in terms of the shift of the $Q_{0-0}$ band. Thus, these observations (particularly (ii), (iv)), and Table 1) indicate that the substituent effect on the shift of the main Q band is nonlinear and regiospecific. In this respect, the most notable observation is that the Q band positions of 16MtPcs lies between those of 8*β*MtPcs and 8αMtPcs. If there is no regiospecificity,

**Table 1.** Spectroscopic Parameters of Metal-Free and Zinc Phthalocyanines in THF

| compd | $\{Q_{x(0-0)} + Q_{y(0-0)}\}$/2 or $Q_{0-0}$/ nm ($10^3$ $cm^{-1}$) | Δ(shift)[a]/ $10^3$ $cm^{-1}$ | splitting[b]/ $10^3$ $cm^{-1}$ | $\Phi_F$ |
|---|---|---|---|---|
| $H_2Pc$[c] | 680.0 (14.71) | 0.00 | 0.74 | 0.60[e] |
| $4\beta H_2Pc$ | 683.5 (14.63) | −0.08 | 0.79 | 0.49 |
| $8\beta H_2Pc$ | 678.0 (14.75) | 0.04 | 0.83 | 0.58 |
| $4\alpha H_2Pc$ | 706.0 (14.16) | −0.55 | 0.65 | 0.07 |
| $8\alpha H_2Pc$ | 751.0 (13.32) | −1.39 | 0.41 | (0.19)[f] |
| $16H_2Pc$ | 719.0 (13.91) | −0.80 | 0.50 | 0.06 |
| ZnPc | 665.5 (15.03) | 0.00 | | 0.30[e] |
| 4βZnPc | 674.5 (14.83) | −0.20 | | 0.42 |
| 8βZnPc | 671.5 (14.89) | −0.14 | | 0.62 |
| 4αZnPc | 696.0 (14.37) | −0.66 | | 0.14 |
| 8αZnPc[d] | 758.0 (13.19) | −1.84 | | (0.62)[f] |
| 16ZnPc | 707.5 (14.13) | −0.90 | | 0.07 |

[a] Shifts are given by either $\{Q_{x(0-0)} + Q_{y(0-0)}\}/2 - 14.71$ (peak position of $H_2Pc$) or $Q_{0-0} - 15.03$ (peak position of ZnPc). [b] Splitting energy between $Q_{x(0-0)}$ and $Q_{y(0-0)}$ in metal-free compounds. [c] Because of low solubility, data for this compound were collected in 1-chloronaphthalene. [d] Because of solution instability, data for this compound were collected in pyridine. [e] In 1-chloronaphthalene. Taken from: Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1–13. [f] These $\Phi_F$ values were obtained using 1,3,3,1′,3′,3′-hexamethylindotricarbocyanine ($\Phi_F = 0.28$) as a standard (Freyer, W.; Teuchner, K *J. Photochem. Photobiol. A: Chem.* **1988**, *45*, 117–121) because of their Q-band positions in the near-IR. However, they appear too large compared with the other values, obtained using ZnPc in 1-chloronaphthalene as a standard (reference in footnote *e*).

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(2) Konami, H.; Hatano, M. *Chem. Lett.* **1988**, 1359.

(3) Brach, P. J.; Grammatica, S. J.; Ossanna, O. A.; Weinberger, L. *J. Heterocycl. Chem.* **1970**, *7*, 1403–1405. $16H_2$- and 16ZnPc were prepared according to: Kobayashi, H.; Matsumoto, K.; Sonoda, T. *Proceedings of the 2nd International Symposium on the Chemistry of Functional Dyes*, Kobe, 1992; Mita Press: Osaka, Japan, 1992; Abstracts, pp 290–295.

(4) All Pcs gave satisfactory elemental analytical data. Details are described in a full paper.

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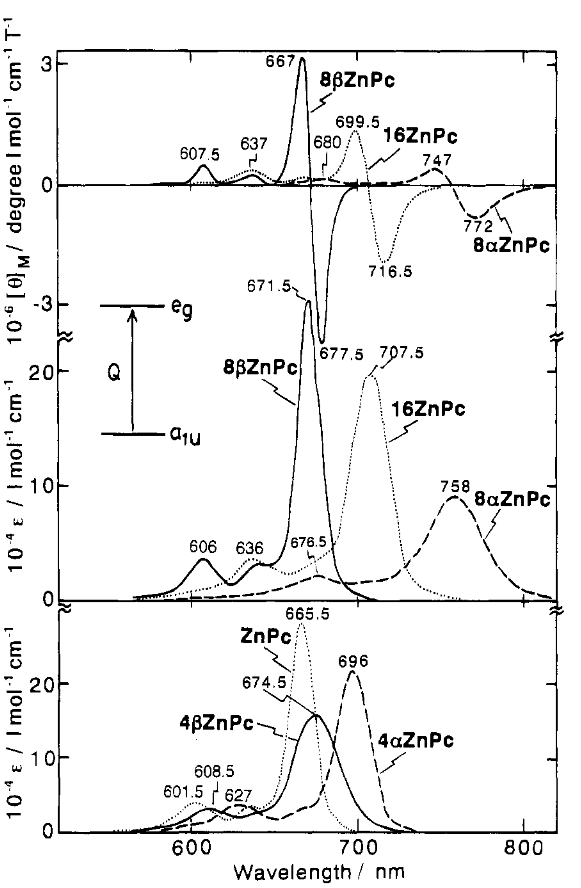

**Figure 1.** Electronic absorption and MCD spectra of zinc complexes in THF in the Q band region (spectra of 8αZnPc recorded in pyridine due to solution instability).

the Q bands of 16MtPcs are conjectured to lie at the longest wavelengths, as explained by citing the case of *tert*-butylated ZnPcs in the introductory part. Because of nonadditivity and regiospecificity, the $Q_{0-0}$ bands of zinc derivatives lie from shorter to longer wavelengths in the order ZnPc, 8$\beta$ZnPc, 4$\beta$ZnPc, 4αZnPc, 16ZnPc, and 8αZnPc, and the energy difference between ZnPc and 8αZnPc becomes more than 1800 cm$^{-1}$.

The metal-free derivatives show split $Q_{0-0}$ bands, conventionally named the $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands.[5] The position of the main Q band, defined as the midenergy between the $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands, shifts similarly toward those of the above zinc derivatives depending on the position and number of alkoxyl groups (Table 1). However, the energy difference between the $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands decreases in the order 8$\beta H_2$Pc > 4$\beta H_2$Pc > $H_2$Pc > 4α$H_2$Pc > 16$H_2$Pc > 8α$H_2$Pc; *i.e.*, alkoxyl groups at $\beta$ positions increase the energy difference while those at α positions reduce it. In other words, alkoxyl groups at $\beta$ positions strengthen the $D_{2h}$ symmetry of the molecule while those at α positions function to weaken it. Interestingly, this order is approximately the same as the above order of the $Q_{0-0}$ band position, indicating that *the energy difference between the* $Q_{x(0-0)}$ *and* $Q_{y(0-0)}$ *bands decreases with decreasing energy of the Q band.*

The above phenomenon of the absorption band position has been observed commonly for the band position of the emission and excitation spectra. For example, the $S_1$ emission peaks appeared at 703, 710, 728, 740, and 783 (plus 809) nm for 8$\beta H_2$-, 4$\beta H_2$-, 4α$H_2$-, 16$H_2$-, and 8α$H_2$Pc, respectively. The Stokes shift is generally very small. The $\Phi_F$ values of MtPcs with substituent groups at the $\beta$ position do not differ markedly from those of unsubstituted MtPcs, but those with groups at the α positions become significantly smaller with the increasing number of alkoxyl groups; in other words, the $\Phi_F$ values become smaller, the lower the energy of the Q band. This implies that $\Phi_F$ becomes smaller with decreasing energy gap between the HOMOs and LUMOs, suggesting that the excited states become unstable in systems showing a Q band at lower energy, plausibly due to the ease of electron transfer. Obviously, the decrease of $\Phi_F$ values is more than linear with respect to the number of alkoxyl groups at α positions. Here again, the $\Phi_F$ values decrease in the order $H_2$Pc > 8$\beta H_2$Pc > 4$\beta H_2$Pc > 4α$H_2$Pc > 16$H_2$Pc, which is the same order as that of the Q-band positions of the above mentioned zinc (Figure 1 and Table 1) and metal-free derivatives (Table 1). In the case of the zinc derivatives, $\Phi_F$ decreases in the order 8$\beta$ZnPc > 4$\beta$ZnPc > ZnPc > 4αZnPc > 16ZnPc.

Of these observations, the shift of the Q band position by alkoxyl groups alone may be explained qualitatively as follows. The Q band corresponds to a transition from the HOMO to the LUMO. Therefore, the red shift can be explained by a decrease of the energy gap ($\Delta E$) between these orbitals. According to the molecular orbital calculations of Pcs so far reported,[6] the LCAO coefficients at α positions of the HOMO ($a_{1u}$ orbital in $D_{4h}$ symmetry) are larger than those at $\beta$ positions so that the attachment of electronegative alkoxyl groups at α positions destabilizes the HOMO level more than for substitution at $\beta$ positions. As a result, the $\Delta E$(HOMO−LUMO) becomes smaller when alkoxyl groups are linked at α positions. The correctness of this argument is supported by the inverse substituent effect of electron-withdrawing groups. For example, it is known that the introduction of four nitro groups at α positions of Pcs shifts the $Q_{0-0}$ band to shorter wavelength by *ca.* 20−30 nm while introduction at $\beta$ positions changes the $Q_{0-0}$ band position negligibly.[7] In this case, $a_{1u}$ type HOMOs are stabilized so that the $\Delta E$(HOMO−LUMO) becomes larger. We examined redox potentials of the zinc complexes. Although, all the first oxidation and reduction potentials did not necessarily change as expected, the $\Delta E$(1st oxidn−1st redn) values generally become smaller for compounds having Q bands at longer wavelengths. The values for Zn-, 4$\beta$Zn-, 8$\beta$Zn-, 4αZn-, 16Zn-, and 8αZnPc were 1.96, 1.72, 1.67, 1.68, 1.61, and 1.38 eV, respectively, in *o*-dichlorobenzene containing 0.3 M tetrabutylammonium perchlorate.

In summary, we have reported that, for five types of alkoxy-substituted MtPcs (Mt = $H_2$ and Zn), the Q band positions (from shorter to longer wavelengths), the magnitudes of the splitting of the $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands in metal-free derivatives, and the $\Phi_F$ values of fluorescence emission change explicitly in the order 8$\beta$MtPc, 4$\beta$MtPc, 4αMtPc, 16MtPc, and 8αMtPc (unsubstituted Pcs lie either first or third in this row). In addition, the changes are not linear with respect to the number and position of the alkoxyl groups. Such systematic and regiospecific and nonlinear spectroscopic properties have not been reported to date for porphyrins and phthalocyanines.

**Supplementary Material Available:** The $S_1$ emission and excitation spectra of metal-free compounds and the Soret absorption spectra of ZnPcs in THF (2 pages). Ordering information is given on any current masthead page.

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