Selective detection of minor prototropic tautomers in low-symmetry tetraazaporphyrin derivatives by the combined use of electronic absorption, MCD, and CI calculations

Kazuyuki Ishii, Hatsumi Itoya, Hideya Miwa and Nagao Kobayashi*

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A series of low-symmetry metal-free tetraazaporphyrin (TAP) derivatives, *i.e.* monobenzo-substituted ($1H_2$), adjacently dibenzo-substituted ($2AdH_2$), oppositely dibenzo-substituted ($2OpH_2$), and tribenzo-substituted ($3H_2$) TAP derivatives, has been investigated by the combined use of electronic absorption, MCD, and CI calculations, proving the existence of two prototropic tautomers in $1H_2$ and $3H_2$.

Recently, various porphyrinic compounds with low-symmetry π-conjugated systems have been investigated, since control of the π-symmetry is a promising route to achieving novel properties.[1–5] The π-symmetry of a porphyrin ring is reduced from D_{4h} symmetry by reduction of the pyrrole ring or conjugation of aromatic rings to the pyrrole rings. In these low-symmetry porphyrins, it is interesting to focus on which pyrrole rings combine with protons. Previous X-ray and electronic absorption studies on tetraazaporphyrin (TAP) derivatives substituted with aromatic ring units indicate that two protons were preferentially bonded to the pyrrole rings with smaller aromatic ring units.[6,7] Therefore, it has been difficult to confirm the existence of the minor prototropic tautomer, where two pyrrole protons are attached to the pyrrole ring having a larger π-conjugated system. The sole example is a phthalocyanine (Pc) derivative, where one of the benzo fragments is replaced by a naphthalene nucleus (Pc_3Nc).[8] Although the existence of two prototropic tautomers was confirmed by an electronic absorption spectrum and spectral hole burning, there was some difficulty in measuring or assigning the tautomers: (1) it is difficult to confirm two tautomers without spectral hole burning at very low temperature and (2) synthetic efforts are required since the position of the protons is predicted by substitution effects.

In this study, we have investigated a series of low-symmetry metal-free TAP derivatives lying structurally between TAP and phthalocyanine, *i.e.* monobenzo-substituted ($1H_2$), adjacently dibenzo-substituted ($2AdH_2$), oppositely dibenzo-substituted ($2OpH_2$), and tribenzo-substituted ($3H_2$) TAP derivatives (Fig. 1), in terms of electronic absorption, magnetic circular dichroism (MCD), and molecular orbital (MO) calculations.[9,10] $1H_2$, $2OpH_2$, and $3H_2$ have two prototropic tautomers, termed X and Y, where two pyrrole protons are bonded to the pyrrole rings in the *X* and *Y* directions, respectively. We have succeeded in proving the existence of the two tautomers in $1H_2$ and $3H_2$ by the combined use of electronic absorption, MCD, and configuration interaction (CI) calculations.

Electronic absorption and MCD spectra of $1H_2$, $2AdH_2$, $2OpH_2$ and $3H_2$ in the Q band region are shown in Fig. 2 (upper and middle). In the electronic absorption spectra, intense Q_x and Q_y bands are seen for each compound. In the MCD spectrum of $2OpH_2$, Faraday *B* terms of opposite sign are observed at 733 and 580 nm, which are attributable to the Q_x (734 nm) and Q_y (581 nm) electronic absorption bands, respectively. In a similar manner, for $2AdH_2$, MCD *B* terms of opposite sign are observed at 677 and 633 nm, which correspond to the Q_x (678 nm) and Q_y (637 nm) absorption peaks, respectively. In contrast, the MCD spectra of $1H_2$ and $3H_2$ are clearly different from those of $2AdH_2$ and $2OpH_2$. In the case of $1H_2$, a dispersion type pseudo-*A* term can be seen at around 650 nm, in addition to the MCD *B* terms at 699 and 594 nm corresponding to the Q_x (701 nm) and Q_y (598 nm) absorption bands, respectively. Although the absorbance decreases in the order 701, 598, and 653 nm, the MCD peak at 656 nm is more intense than that at 699 nm, directly indicating the existence of degenerate transitions. In a similar manner, a pseudo-*A* term of $3H_2$ can be observed at around 670 nm, in addition to the MCD *B* terms of the Q_x (707 nm) and Q_y (610 nm) bands. These features were not observed in the corresponding Zn, Mg, and Pd complexes.[10]

In order to clarify the pseudo-*A* term, CI calculations were carried out using the ZINDO/S method.[10–12] The electronic absorption spectra of these zinc complexes were well reproduced by the CI calculations,[10] indicating that the structures and parameters used in the calculations are reliable. Therefore, CI calculations of these metal-free compounds were carried out using the same structures and parameters as the zinc complexes. The CI calculation results are shown in Fig. 2 (lower). Since the observed Q_x and Q_y bands of $2AdH_2$ were closely reproduced by the calculated bands at 680 and 653 nm, our calculations are plausible. In the case of $1H_2$, the Q_x and Q_y bands calculated for $1H_2X$ are clearly different from those calculated for $1H_2Y$. The calculated Q_x (721 nm) and Q_y (603 nm) bands of $1H_2X$ are in agreement with the absorption peaks at 701 and 598 nm, respectively. On the other hand, the calculated Q_x and Q_y bands (656, 654 nm) of $1H_2Y$ are almost entirely degenerate, which reproduces the pseudo-*A* term corresponding to the absorption peak at 653 nm. This degeneracy can explain the intense MCD peak at 656 nm, since the MCD intensity increases with decreasing energy difference between the Q_x and Q_y bands.[13]

In $3H_2X$, the Q_x and Q_y bands were calculated at 711 and 630 nm, which reproduces well the absorption peaks at 709 and

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Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.
E-mail: nagaok@mail.tains.tohoku.ac.jp; Fax: +81-22-795-7719;
Tel: +81-22-795-7719

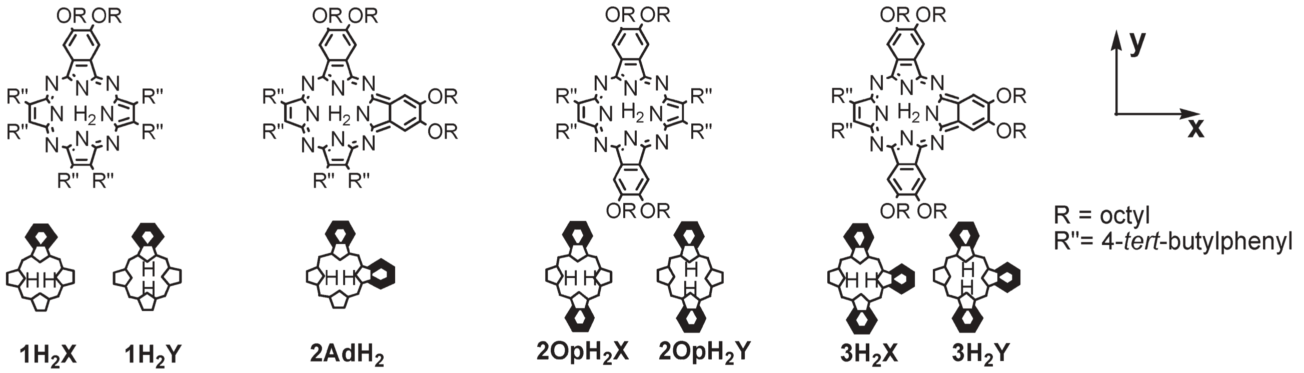

Fig. 1 Molecular structures of $1H_2$, $2AdH_2$, $2OpH_2$, and $3H_2$.

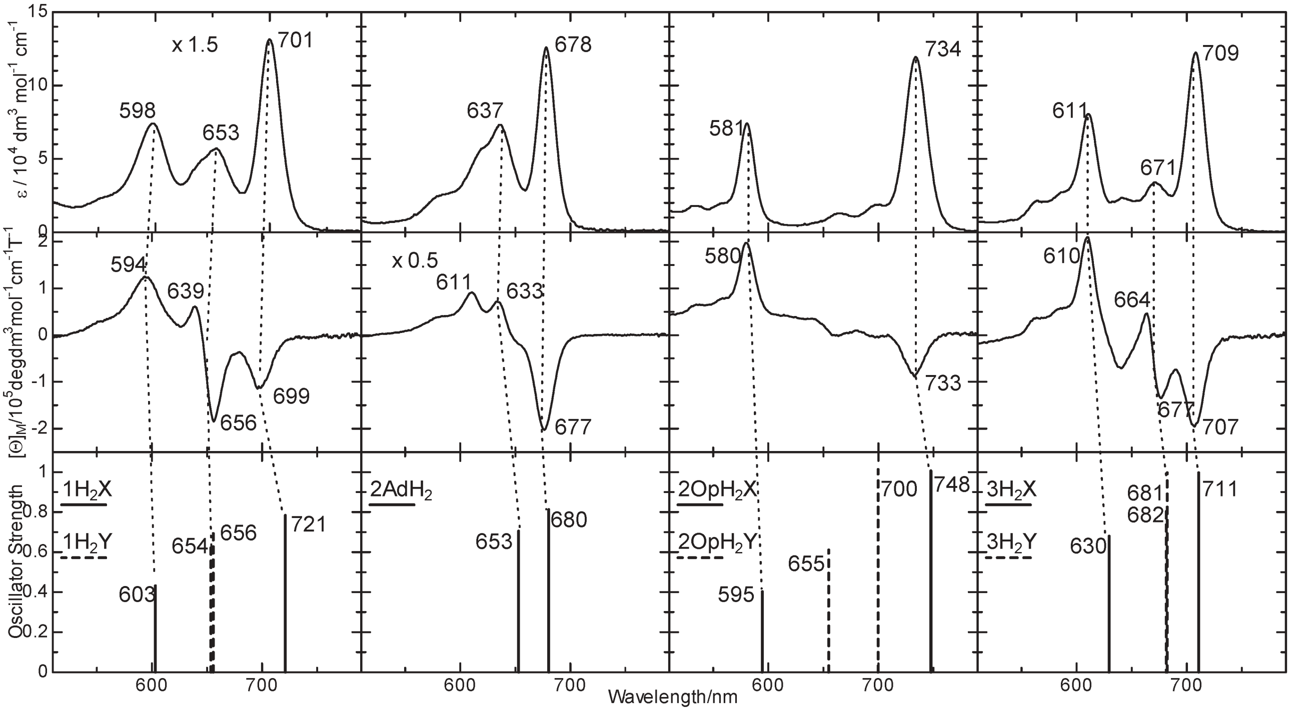

Fig. 2 Electronic absorption (upper), MCD (middle), CI calculation (lower) spectra of $1H_2$, $2AdH_2$, $2OpH_2$, and $3H_2$.

611 nm, respectively. Similarly to $1H_2$, degenerate Q_x and Q_y bands were calculated at 681 and 682 nm for $3H_2Y$. While the absorption band at 671 nm appears to be vibronic, the pseudo-*A* term in the MCD spectrum clearly proves the existence of $3H_2Y$. The calculated Q_x (748 nm) and Q_y (595 nm) bands of $2OpH_2X$ reproduce well the absorption peaks at 734 and 581 nm, respectively. The Q_x (700 nm) and Q_y (655 nm) bands of the Y tautomer appear to be observed in the electronic absorption spectrum. However, negative/positive MCD *B* terms cannot be seen corresponding to the calculated Q_x (700 nm) and Q_y (655 nm) bands, which suggests that the Y tautomer is very minor or absent in the ground state.

The calculated state-energies also support the experimental results.[11] The energy differences (ΔE_{XY}) between the X and Y tautomers in the ground state were evaluated as −1200, −2900, and −1700 cm^{-1} for $1H_2$, $2OpH_2$, and $3H_2$, respectively, indicating that the X tautomers are more stable. The ΔE_{XY} value of $2OpH_2$ is twice those of $1H_2$ and $3H_2$. This is consistent with the experimental result that the minor Y tautomers could be detected only in $1H_2$ and $3H_2$, and not in $2OpH_2$. In addition, calculations on pyrrole deprotonated dianionic species show that the negative charge density on the nitrogen atoms along the *X*-axis is larger than that along the *Y*-axis.[11] Thus, the fused benzene rings decrease the proton affinity of the pyrrolic nitrogens, which makes the X tautomer a major component.

In summary, we have investigated low-symmetry metal-free TAP derivatives, and shown that in $1H_2$ and $3H_2$, the X and Y tautomers exist as major and minor components, respectively. We have demonstrated the effectiveness of the combined use of electronic absorption, MCD, and CI calculations for proving the existence of minor components of porphyrinic compounds. When using this method, it is important to analyze the corresponding zinc complexes for reliability of the structures and parameters.

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