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Rotational deviation of 3-acetyl group from cyclic tetrapyrrole π-plane in synthetic bacteriochlorophyll-*a* analogs by 20-substitution

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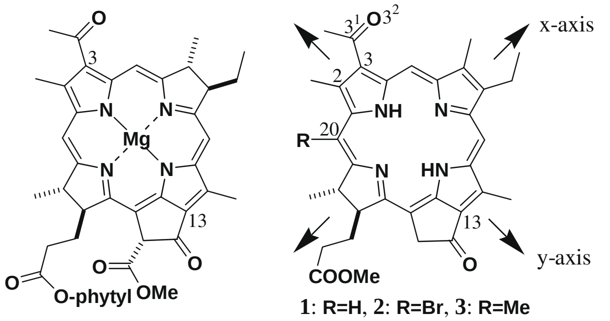
ABSTRACT

The 3-acetyl groups of synthetic methyl pyropheophorbides were rotated around the 3–3[1] bond and the rotational conformers were obtained in a dichloromethane solution of 20-bromo- and methyl-substituted compounds, based on their electronic and vibrational absorption spectra. Such a rotational deviation of the 3-acetyl group from the cyclic tetrapyrrole plane induced less π-conjugation to affect the redmost Q_y band, which has been observed in natural photosynthetic antenna systems, bacteriochlorophyll-*a* molecules in oligopeptides.

Electronic absorption spectra of naturally occurring chlorophylls (Chls) and bacteriochlorophylls (BChls) are one of the key factors in photosynthetic light-harvesting (LH) and energy-migrating antennas as well as electron-transferring reaction centers.[1–3] Especially, the absorption bands at the longest wavelength, redmost (Q_y) bands, determine the singlet excited energy and the absorption maxima of (B)Chls in the natural apparatus are called 'site energy'. The Q_y maxima were partially affected by their surrounding environments and mainly determined by their molecular structures including peripheral substituents. In the same π-conjugated systems (porphyrin, chlorin, and bacteriochlorin), the 3-substituents primarily regulated the Q_y maxima of photosynthetically active (B)Chls (Fig. 1):[1] for example, Chls-*a*/*d* possessing the 3-vinyl/formyl groups gave their maxima at 662/689 nm in acetone.[4] In natural antenna systems, the same (B)Chl molecules gave different site energies, which provided an energetic gradient for efficient energy migration. The energy difference is created by environmental proteins: coordination with the central magnesium, hydrogen-bond with the carbonyl group at the 3- and 13-positions, and so on.[5]

Purple photosynthetic bacteria usually have LH2 as their main peripheral antenna.[5] LH2 had the most intense absorption band at 850 nm (B850), which was ascribable to the Q_y band of oligomeric BChls-*a* (see left of Fig. 1). Some purple bacteria produce LH3 instead of LH2.[5] The alternative LH3 gave a Q_y maximum at 820 nm (B820), although the two were almost the same supramolecular structures of proteins with BChls-*a*. The difference in absorption bands was due to the conformation of the 3-acetyl group. X-ray crystallographic analyses clearly indicated all the acetyl groups in B850 were more planar to the cyclic tetrapyrrole π-systems in a molecule than those in B820: their deviations were about 20° and 50° for B850 and B820, respectively.[5,6] It is theoretically and experimentally known that such a larger and smaller π-conjugation of the 3-substituents shifted Q_y bands to a longer and shorter wavelength, respectively.[7–11] In FMO proteins as minor antenna systems of green sulfur bacteria, site energies of composite BChls-*a* were proposed to be similarly regulated by rotational conformation of the 3-acetyl groups.[11,12] Here, we report on a similar regulation of Q_y bands of methyl pyropheophorbides **1**–**3** (see right of Fig. 1) possessing the 3-acetyl group as synthetic BChl-*a* analogs



1: R=H, **2**: R=Br, **3**: R=Me

Figure 1. Molecular structures of natural bacteriochlorophyll-*a* (left) and the synthetic analogs **1**–**3** (right).

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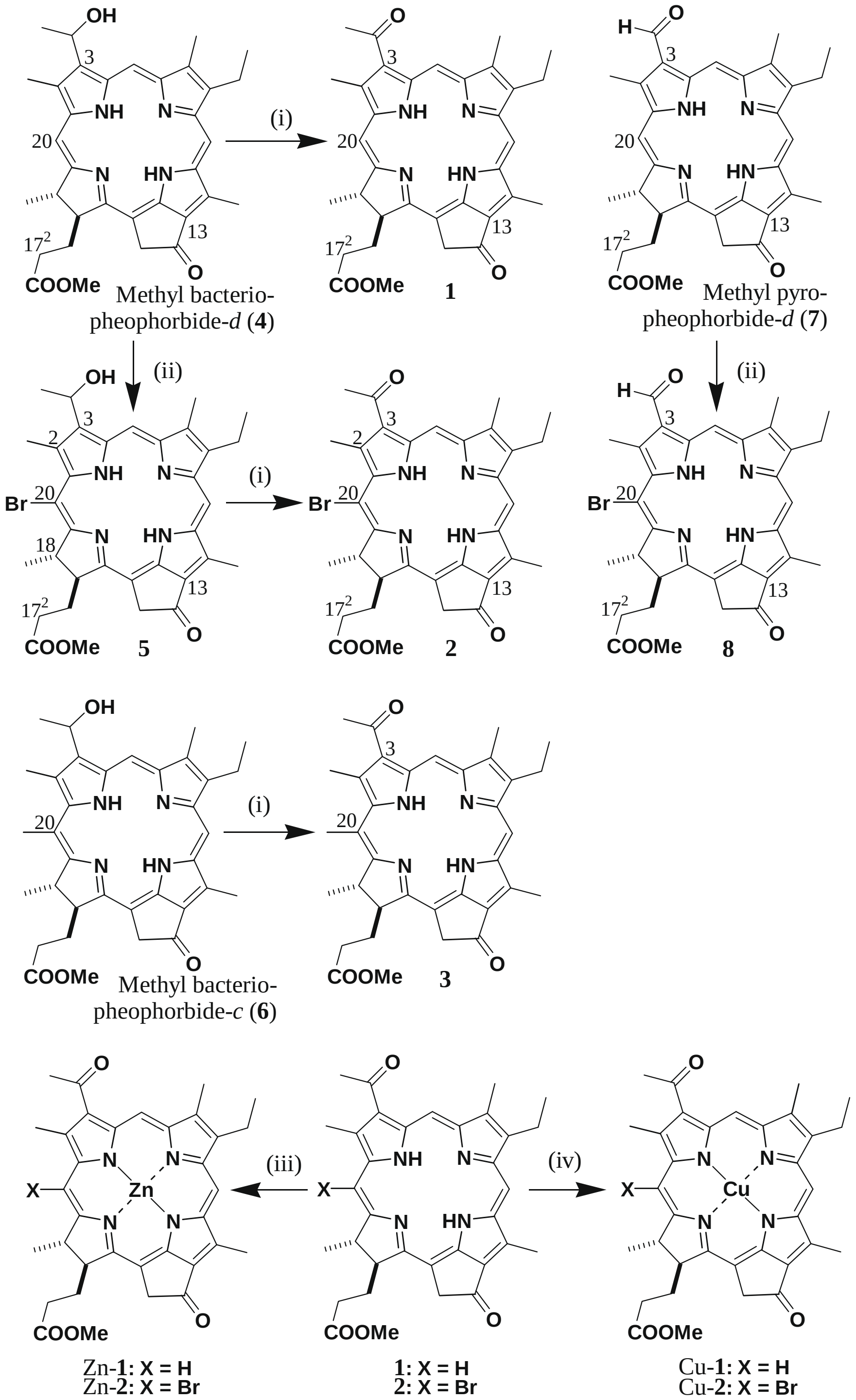
in dichloromethane. This is the first experimental evidence, to our best knowledge, of such rotational conformers of chlorophyllous pigments in a solution.

All compounds examined here were prepared by modifying Chl-*a* and BChl-*c* as shown in Scheme 1 and the experimental details are reported in Supplementary data.

Methyl bacteriopheophorbide-*d* (**4**) possessing 1-hydroxyethyl group at the 3-position was dissolved in dichloromethane to give electronic absorption bands at the full visible region (see the dotted line of Fig. 2b).[13] The most intense band at 410 nm was called Soret band and several bands at a region of longer wavelength than the Soret peak were termed *Q* bands. The four peaks at 505, 536, 604, and 660 nm were observed as the *Q* bands and assigned to $Q_x(0,1)$, $Q_x(0,0)$, $Q_y(0,1)$, and $Q_y(0,0)$, respectively (see Table 1). The subscription *x* and *y* indicate the directions of transition dipole moments in the bands (see Fig. 1). The redmost $Q_y(0,0)$ band was more intense than any other *Q* bands, which was characterized in chlorin chromophores.[14] Its sharpness clearly indicates compound **4** to be monomeric in a diluted dichloromethane solution: the full width at a half maximum = 360 cm^{-1}.



Scheme 1. Synthesis of methyl pyropheophorbides by modifying methyl bacteriopheophorbides-*c* and *d* as well as methyl pyropheophorbide-*d*: (i) Pr_4RuO_4–$O(CH_2CH_2)_2N(O)Me/CH_2Cl_2$; (ii) $C_5H_5NH^+Br_3^-/CH_2Cl_2$; (iii) $Zn(OAc)_2{\cdot}2H_2O/MeOH$–$CH_2Cl_2$; (iv) $Cu(OAc)_2{\cdot}H_2O/MeOH$–$CH_2Cl_2$.