Uncovering the mechanism for selective control of the visible and near-IR absorption bands in bacteriochlorophylls a, b and g

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Bacteriochlorophylls (BChls) play an important role as light harvesters in photosynthetic bacteria. Interestingly, bacteriochlorophylls (BChls) a, b, and g selectively tune their visible (Qx) and near IR (Qy) absorption bands by the substituent changes. In this paper, we theoretically study the mechanism for the selective control of the absorption bands. Density functional theory (DFT) and time-dependent DFT (TD-DFT) and four-orbital model analyses reveal that the selective red-shift of the Qy band with the substituent change from BChl a to b occurs with the lower-energy shift of the (HOMO, LUMO) excited state directly induced by the molecular-orbital energy changes. In contrast, the Qx band hardly shifts by the cancellation between the higher- and lower-energy shifts of the (HOMO-1, LUMO) excited state directly induced by the molecular-orbital energy changes and configuration interaction, respectively. On the other hand, with the substituent changes from BChl a to g, the Qy band selectively blue-shifts by the larger higher-energy shift of the (HOMO-1, LUMO) excited state directly induced by the molecular-orbital energy shifts than the lower-energy shift due to the configuration interaction. In contrast, the Qx band hardly shifts by the cancellation between the higher- and lower-energy shifts of the (HOMO, LUMO) excited state directly induced by the molecular-orbital energy changes and configuration interaction, respectively. Our work provides the important knowledge for understanding how nature controls the light-absorption properties of the BChl dyes, which might be also useful for design of porphyrinoid chromophores.

Key words: bacteriochlorophylls, selective absorption control, density functional theory, four-orbital model

Bacteriochlorin chromophores play a crucial role as light absorbers in photosynthetic bacteria. In addition, bacteriochlorin dyes have been used as photosensitizers for photodynamic therapy. So far, three kinds of naturally synthesized bacteriochlorin chromophores, called bacteriochlorophylls (BChls) a, b, and g have been discovered. These BChl chromophores have a bacteriochlorin ring fused with cyclopentanone on the pyrrole ring C having a magnesium central ion, as shown in Figure 1. The BChls contain different peripheral substituents on the rings A, B, and D, as shown in Figure 2. By the substituent changes, the BChls selectively tune their visible (Qx) and near IR (Qy) absorption bands, as shown in Figure 3. For instance, by the dehydrogenation at the 8 and 8′ positions on the ring B, the Qx band in BChl a remarkably red-shifts in BChl b with a slight red-shift of the Qy band. In addition, by both the dehydrogenation on the ring B and the replacement of the acetyl group on the ring A with a vinyl group, the Qx band in BChl a blue-shifts in BChl g with a slight blue-shift of the Qy band. This result suggests that nature successfully tunes the Qx and Qy bands.
Figure 1  Fundamental skeleton of BChls \( a \), \( b \), and \( g \).

Figure 2  Molecular structures of BChls \( a \), \( b \) and \( g \) and an \( L \)-histidine-residue analog (His) for the axial ligand (bottom right).

Figure 3  Schematic picture of the selective shifts of \( Q_y \) and \( Q_x \) absorption bands. Experimental peak energies and relative intensities of BChls \( a \), \( b \) and \( g \) in diethyl ether are reported in Ref. 2.
selectively by the substituent changes. In order to get an insight into the mechanism, theoretical investigations are required. So far, the light-absorption properties of the BChl $a$, $b$, and $g$ have been studied with several quantum chemical calculations. 4–8 Linnanto et al. reported the $Q_x$ and $Q_y$ excitation energies of BChls $a$, $b$ and $g$ calculated by semi-empirical quantum chemical calculations. 5,6 Their calculations reproduced the selective red-shift of the $Q_y$ band with the substituent change from BChl $a$ to $b$. 4 On the other hand, their calculations failed to reproduce the selective blue-shift of the $Q_x$ band from BChl $a$ to $g$. 5,6 Furthermore, the mechanism of the selective tuning has not been clarified yet. In this paper, we theoretically study the mechanism with density functional theory (DFT) and time-dependent DFT (TD-DFT) and four-orbital model analyses.

Computational Details

The molecular structures in the ground states were optimized using DFT calculations with the B3LYP functional and 6-31G(d) basis set. With the optimized structures, absorption spectra were computed with TD-DFT calculations at the B3LYP/6-31G(d) level of theory. In the calculations of the optimized structures and excited states, the conductor-like polarizable continuum model (CPCM) was used to take into account solvent effects of diethyl ether, which was used in the previous experiments. All calculations were performed with Gaussian 09 software. DFT and TD-DFT calculations with the similar functional and basis set were reported to be sufficiently appropriate to study the properties of excited states and molecular orbitals of the BChl dyes. 7,8

Results and Discussion

Models of BChls

Since most of the BChl molecules in photosynthetic bacteria are coordinated with a histidine residue as a fifth ligand from surrounding proteins, we have studied BChls $a$, $b$ and $g$ coordinated with an $L$-histidine-residue analog (His) (Fig. 2). In addition, as pointed out by Oba et al. and Balaban,

Figure 4 Optimized structures of BChls $a$, $b$ and $g$ coordinated with His from the face or back side obtained by DFT calculations. Gray: carbon, white: hydrogen, blue: nitrogen, red: oxygen, yellow: magnesium atoms.
the axial ligand is coordinated to the central magnesium ion from the face (β-coordination) or back side (α-coordination) with respect to the BChl ring. Therefore, we examined the BChls a, b and g coordinated with His from the face or back side.

**Optimized Structures**

Figure 4 shows the optimized structures of BChls a, b and g coordinated with His from the face or back side. The bacteriochlorin rings are planar for all the BChls. The His ligand is coordinated with the central magnesium ion almost perpendicularly. The central magnesium ion is located slightly above or below the bacteriochlorin ring by the face- or back-side ligation, respectively. The bond length between the magnesium ion and the coordinating nitrogen atom of His was estimated to be 2.17 Å for face- and back-His-BChl a, face- and back-His-BChl b, and face-His-BChl g and the one for back-His-BChl g to be 2.18 Å. From X-ray single crystal structure analyses, the bond length between the Mg ion and N atom of a histidine residue was reported to be 2.27 and 2.32 Å for B850 BChl a pairs. Our estimated bond lengths are comparable to the experimental data, indicating the validity of the optimized structures.

**Molecular-Orbital Shifts**

Figure 5 shows the electronic distributions and energies of the second highest occupied molecular orbital (HOMO-1), highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and second lowest unoccupied molecular orbital (LUMO+1) of BChls a, b and g coordinated with His from the face or back side. This figure shows that the certain molecular orbitals are selectively shifted by the substituent changes. From BChl a to b, the energy of HOMO increases by 0.05 (face and back) eV and LUMO+1 decreases by 0.21(face)/0.19(back) eV. In contrast, the HOMO-1 and LUMO hardly shift. On the other hand, as compared to BChl b, the HOMO, LUMO, and LUMO+1 levels in BChl g are elevated by 0.09(face)/0.10(back) eV, 0.19(face)/0.20(back) eV, and 0.13(face)/0.12(back) eV, respectively, and the HOMO-1 energy just slightly increases by 0.04 eV (face and back). These selective molecular-orbital shifts are associated to the changes in

![Figure 5](image-url)
the electronic distributions by the substituent variations on
the rings A and B. Since those molecular orbitals have no
electronic distributions on the longer alkyl chains (phytyl
and farnesyl) on the ring D, the difference in the alkyl chain
has almost no effects on the molecular-orbital shifts. In addition,
no remarkable dependence of the direction of the axial
ligation is confirmed. As shown by red circles in Figure 5,
the HOMO and LUMO+1 in BChls b and g are delocalized
on the ethylidene substituent by the dehydrogenation on the
ring B. On the other hand, as shown by blue circles in Figure
5, the replacement of the acetyl group to a vinyl group causes
delocalization of the HOMO, LUMO, and LUMO+1 on the
vinyl group in BChl g.

The selective molecular-orbital shifts are explained by the
electronic distributions in BChl a on the rings A and B. For
the dehydrogenation from BChl a to b, the electronic distribu-
tions on the carbon atoms at the 8 and 8′ positions are important. As shown in Figure 6a, the HOMO and LUMO+1 in BChl a have discernible electronic distributions at the 8 and 8′ positions, which give rise to above mentioned remark-
able delocalizations in BChls b and g. In contrast, the
HOMO-1 and LUMO in BChl a have no electronic distribu-
tions on the moiety, providing their little response to the
structural change. On the other hand, for the substitution
change on the ring A, electronic distributions on the carbon
atoms at the 3 and 3′ positions and neighboring oxygen atom
are crucial. As shown in Figure 6b, the HOMO, LUMO, and
LUMO-1 in BChl a are remarkably distributed on the acetyl
group in contrast to the HOMO-1. The distributions of the
HOMO, LUMO, and LUMO+1 on the acetyl group are con-
sistent with the selective shifts of those molecular orbitals in
BChl g.

The molecular-orbital shifts occur with the following
mechanisms. For the dehydrogenation, the HOMO and
LUMO+1 in BChl a are considered to be shifted by interac-
tions with an additional ethylene group. As shown by the left
figure in Figure 7a, the HOMO and LUMO+1 levels in BChl
a interact with the HOMO (π orbital) and LUMO level (π*
orbital) of the hypothetical methyl ethylene group, respec-
tively. In consequence, the HOMO and LUMO+1 levels in
BChl b are elevated and lowered, respectively. In fact, the
anti-bonding and bonding interactions for HOMO and
LUMO+1 in BChl b, respectively, are displayed by red cir-
cles in the right side in Figure 7a. On the other hand, the
selective molecular-orbital shifts with the substituent
replacement from BChl b to g are attributed to the difference
in the electronic property between acetyl and vinyl groups.
As shown in Figure 7b, an acetyl group has an electron with-
drawing property that stabilizes the molecular orbitals. On
the other hand, a vinyl group has no electron withdrawing
property. Therefore, the replacement of the acetyl group
with the vinyl group destabilizes the HOMO, LUMO, and
LUMO+1 having the electronic distributions on the acetyl
Figure 6 Magnified pictures of molecular orbitals (|isovalue|=0.02) of BChl a coordinated with His from the face side on the (a) ring B and (b) ring A.
shifts are larger than the experimental ones (0.050 and 0.035 eV), the calculations qualitatively reproduce the experimentally reported selective absorption shifts (Fig. 3). In addition, our calculations indicate that the back-side coordination systematically shows the slightly red-shifted Qy and Qx bands as compared to the face-side one.

Linnanto et al. reported the Qy and Qx excitation energies of BChls a, b and g calculated by semi-empirical quantum chemical calculations. Their calculations reproduced the selective red-shift of the Qy band with the substituent change from BChl a to b. On the other hand, their calculations showed that with the substituent changes from BChl a to g the Qy band more largely blue-shifts than the Qx band inconsistent with the experimental result. They also calculated the Qx and Qy excitation energies of 1:1 complexes of the BChl dyes with a solvent molecule. The complexation with a solvent molecule failed to reproduce the selective absorption shifts of the Qx and Qy bands not only from BChl a to g, but also from BChl a to b. On the other hand, our TD-DFT calculations well reproduced the selective absorption shifts from

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**Figure 7** Mechanism of molecular-orbital shifts. (a) Dehydrogenation on the ring B and (b) substituent change on the ring A.

**Figure 8** Calculated excitation spectra of BChls a, b and g coordinated with His from the face (red lines) or back (blue lines) side.
BChl \( a \) to \( b \) and from BChl \( a \) to \( g \), as shown in Figure 8.

Table 1 shows the configurations of the \( Q_y \) and \( Q_x \) absorption bands in BChls \( a \), \( b \) and \( g \). The \( Q_y \) excited states in BChls \( a \), \( b \) and \( g \) are predominantly attributed to the lowest (HOMO, LUMO) excited state with a minor contribution of the fourth lowest (HOMO-1, LUMO+1) excited state. On the other hand, the \( Q_x \) excited states are dominated by the second lowest (HOMO-1, LUMO) excited state partially mixed with the third lowest (HOMO, LUMO+1) excited state. The mixings between the excited states take place by the configuration interaction based on electron repulsion between the corresponding excited states. The assignments of the \( Q_y \) and \( Q_x \) transitions are consistent with those based on the Gouterman’s four-orbital model\(^2\,^18\), supporting the validity of our calculation results. The contribution of the HOMO-1 \( \rightarrow \) LUMO+1 transition in the \( Q_y \) transition very slightly increases from 3% (face, back) in BChls \( a \) and \( b \) to 4% (face, back) in BChl \( g \). On the other hand, the contribution of the HOMO-1 \( \rightarrow \) LUMO+1 in the \( Q_x \) transition more strikingly increases from 6% (face and back) in BChl \( a \) to 9% (face)/8% (back) in BChl \( b \), 13% (face, back) in BChl \( g \), indicating the enhancement of the configuration interaction for the \( Q_x \) band from BChl \( a \) to \( b \), \( g \).

### Four-Orbital Model Analysis

In order to analytically understand the selective absorption shifts, we examined the calculation results with the four-orbital model\(^1\,^3\,^18\). The schematic energy-level diagrams of the four-orbital model are shown in Figures 9a and 9b. From Figure 9a, we can see that there exist four electroni-
between the BChls, as shown in Figure 10b. Because of the symmetry, the (HOMO, LUMO) and (HOMO−1, LUMO+1) excited states interact with each other by configuration interactions and the (HOMO−1, LUMO) and (HOMO, LUMO+1) excited states do so, as shown in Figure 9b. The Hamiltonian matrices, eigenfunctions of \(Q_y\) and \(Q_x\) excited states and mixing coefficients are expressed by the following equations.

\[
|1 \rangle = |\text{HOMO, LUMO} \rangle \quad (1)
\]
\[
|2 \rangle = |\text{HOMO−1, LUMO} \rangle \quad (2)
\]
\[
|3 \rangle = |\text{HOMO, LUMO+1} \rangle \quad (3)
\]
\[
|4 \rangle = |\text{HOMO−1, LUMO+1} \rangle \quad (4)
\]

\[
H_{14} = \begin{bmatrix} E_1 & V_{14} \\ V_{14} & E_4 \end{bmatrix}
\]

\[
H_{23} = \begin{bmatrix} E_2 & V_{23} \\ V_{23} & E_3 \end{bmatrix}
\]

\[
|Q_y \rangle = \cos \theta |1 \rangle + \sin \theta |4 \rangle \quad (7)
\]
\[
|Q_x \rangle = \cos \phi |2 \rangle + \sin \phi |3 \rangle \quad (8)
\]

\[
\sin^2 \theta = \frac{1}{2} \left[ 1 - \left( 1 + 4 \left( \frac{V_{14}}{E_1 - E_4} \right)^2 \right)^{1/2} \right] \quad (9)
\]
\[
\sin^2 \phi = \frac{1}{2} \left[ 1 - \left( 1 + 4 \left( \frac{V_{23}}{E_2 - E_3} \right)^2 \right)^{1/2} \right] \quad (10)
\]

in which \(E_i\) is the energy of the \(|i\rangle\) state and \(V_{ij}\) is the off-diagonal element of the configuration interaction between \(|i\rangle\) and \(|j\rangle\) states, \(\langle i | H_{c} | j \rangle\). Assuming that the \(E_i\) value is approximated to be the energy difference between the relevant molecular orbitals, the energy differences of \(E_2-E_1\) and \(E_3-E_2\) and the magnitude of \(V_{ij}\) for the \(Q_y\) and \(Q_x\) transitions were estimated from Figure 5 and by using the mixing coefficients in Table 1 and eqs 9 and 10, respectively. As shown in Figure 10a, from BChl \(a\) to \(b\) and \(g\), the \(E_2-E_1\) and \(E_3-E_2\) values systematically decrease. In particular, the latter energy difference responsible to the \(Q_x\) band more drastically reduces as compared with the former one. The magnitude of the configuration interaction has no remarkable difference between the BChls, as shown in Figure 10b. Thus, the remarkable increase of the mixing coefficient for the \(Q_x\) excited state mainly results from the enhancement of the configuration interaction due to the reduction of the responsible \(E_3-E_2\) energy gap in the denominator of eq 10. The energies of the \(Q_y\) and \(Q_x\) excited states are given by the following equations.

\[
E_{Q_y} = E_i + \Delta E_{Q_y} \quad (11)
\]
\[
E_{Q_x} = E_i + \Delta E_{Q_x} \quad (12)
\]

\[
\Delta E_{Q_y} = - \frac{1}{2} \left( E_2 - E_1 \right) + \frac{1}{4} \left( E_1 - E_4 \right)^2 + V_{14}^2 \quad (13)
\]
\[
\Delta E_{Q_x} = - \frac{1}{2} \left( E_2 - E_1 \right) + \frac{1}{4} \left( E_2 - E_3 \right)^2 + V_{23}^2 \quad (14)
\]

The first and second terms in eqs 11 and 12 are the energy shifts that are directly induced by the molecular-orbital shifts.
and configuration interactions, respectively. Eqs 11–14 for the energy eigenvalues are derived by diagonalization of the Hamiltonian matrices (Eqs 5 and 6). By using the above estimated values of the configuration interactions and energy gaps, the energies of the Q and Q excited states are obtained, as shown in Figure 11. We found that the selective shifts of the Q and Q absorption bands are qualitatively reproduced by the four-orbital model, indicating the sufficient validity of the above-mentioned assumption. The slightly large difference for the Q excitation energy between the TD-DFT and four-orbital model calculations is considered to result from the configuration interaction with higher-energy excited states, as implied in Table 1. Figure 12 shows the first (E and E) and second (ΔE and ΔE) terms of eqs 11 and 12 in the BChls. As shown in Figure 12, the shift of the Q band from BChl a to b is mainly attributed to the reduction in the E energy by the molecular-orbital shift. The invariance of the Q energy is explained by the cancellation between the higher-energy shift of the (HOMO-1, LUMO) excited state by the molecular-orbital shifts and the lower-energy shift by the configuration interaction. Similarly, for the Q band in BChl g, the higher-energy shift of the (HOMO, LUMO) excited state by the molecular-orbital shifts is cancelled with the lower-energy shift by the configuration interaction, retaining the excitation energy. On the other hand, for the Q band in BChl g, similar cancellation also happens, but the higher-energy shift of the (HOMO-1, LUMO) excited state by the molecular-orbital shifts overcomes the lower-energy shift by the configuration interaction, leading to the blue shift. Therefore, based on the four-orbital model analysis, it is found that the selective tuning of the visible and near IR absorption bands is realized by the three mechanisms, as summarized in Table 2.

**Conclusion**

In summary, we have theoretically studied the selective absorption shifts of the Q and Q bands in BChls a, b and g coordinated with the His ligand by DFT and TD-DFT and four-orbital model analyses. TD-DFT analyses successfully reproduced the experimentally reported selective absorption

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**Figure 11** Comparison of Q and Q excitation energies between TD-DFT calculations (blue) and four-orbital model based calculations (red) for BChls a, b and g coordinated with His from the face (open circles) or back (open squares) side.

**Figure 12** E (red), E (red), ΔE (blue), and ΔE (blue) of BChls a, b and g coordinated with His from the face (open circles) or back (open squares) side.

**Table 2** Mechanism for selective tuning of the visible and near IR absorption bands in BChls

| BChl a to b or a to g | E1 or E2 | Configuration interaction | Shift |
|----------------------|----------|---------------------------|-------|
| Qy                   | –        | Cancellation              | Red   |
| Qx                   | +        | Cancellation              | None  |
| Qy                   | +        | Cancellation              | None  |
| Qx                   | Large +  | Partial cancellation      | Blue  |

+ and – stand for higher and lower energy shifts, respectively.
shifts of the Q_y and Q_x bands with the substituent changes from BChl a to b and from BChl a to g. By the analysis based on the four-orbital model, we found that the selective red-shift of the Q_y band from BChl a to b is caused by the lower-energy shift of the (HOMO, LUMO) excited state directly induced by the molecular-orbital energy changes. The Q_y band hardly shifts with the substituent change as a result of the cancellation between the higher- and lower-energy shifts of the (HOMO-1, LUMO) excited state directly induced by the molecular-orbital energy changes and configuration interaction, respectively. On the other hand, the Q_x band selectively blue-shifts from BChl a to BChl b by the larger higher-energy shift of the (HOMO-1, LUMO) excited state directly induced by the molecular-orbital energy changes than the lower-energy shift due to the configuration interaction. In contrast, the Q_y band hardly shifts by the cancellation between the higher- and lower-energy shifts of the (HOMO, LUMO) excited state directly induced by the molecular-orbital energy changes and configuration interaction, respectively. The molecular orbital shifts were qualitatively explained on the basis of the molecular-orbital theory. Our results manifest the high level control of the molecular-orbital energies and configuration interactions in nature for the selective light-absorption tailoring. This knowledge could be also useful for designing new porphyrinoid dyes.

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**References**

1. Scheer, H. *Chlorophylls* (CRC Press, Boca Raton, 1991).
2. Mimuro, M., Kakitani, T. & Tamiaki, H. *Chlorophylls Structure, Reaction and Function* (Shokabo, Tokyo, 2011).
3. Ormond, A. B. & Freeman, H. S. *Dye Sensitizers for Photodynamic Therapy*. *Materials* 6, 817–840 (2013).
4. Thompson, M. A. & Fajer, J. Calculations of bacteriochlorophyll g primary donors in photosynthetic heliobacteria. How to shift the energy of a phototrap by 2000 cm⁻¹. *J. Phys. Chem.* 96, 2933–2935 (1992).
5. Linnanto, J. & Korppi-Tommola, J. Spectroscopic Properties of Mg–Chlorin, Mg–Bacteriochlorin, and Bacteriochlorophylls a, b, c, d, e, f, g, and h Studied by Semiempirical and ab Initio MO/CI Methods. *J. Phys. Chem.* A 105, 3855–3866 (2001).
6. Linnanto, J. & Korppi-Tommola, J. Semiempirical PM5 Molecular Orbital Study on Chlorophylls and Bacteriochlorophylls: Comparison of Semiempirical, ab Initio, and Density Functional Results. *J. Comput. Chem.* 25, 123–138 (2004).
7. Sundholm, D. A. A Density-Functional-Theory Study of Bacteriochlorophyll b. *Phys. Chem. Chem. Phys.* 5, 4265–4271 (2003).
8. Song, J., Gao, F. & Liang, W. Z. How does the Nonlocal HF Exchange Influence the Electron Excitation of Bacteriochlorophyll and its Assembly. *Comput. Theor. Chem.* 965, 53–59 (2011).
9. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 140, A1133–A1138 (1965).
10. Beeke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* 98, 5648–5652 (1993).
11. Marques, M. A. L. & Gross, E. K. U. Time-Dependent Density Functional Theory. *Annu. Rev. Phys. Chem.* 55, 427–455 (2004).
12. Barone, V. & Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* 102, 1995–2001 (1998).
13. Cossi, M., Rega, N., Scalmani, G. & Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. *J. Comput. Chem.* 24, 669–681 (2003).
14. Frisch, M. J. *et al.* Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
15. Oba, T. & Tamiaki, H. Which Side of the π-Macrocycle Plane of (Bacterio)chlorophylls is Favored for Binding of the Fifth Ligand? *Photosynth. Res.* 74, 1–10 (2002).
16. Balaban, T. S. Relevance of the Diastereotopic Ligation of Magnesium Atoms of Chlorophylls in the Major Light-Harvesting Complex II (LHC II) of Green Plants. *Photosynth. Res.* 86, 251–262 (2005).
17. Koepke, J., Hu, X., Muenke, C., Schulten, K. & Michel, H. The Crystal Structure of the Light-Harvesting Complex II (B800–850) from Rhodospirillum Molischianum. *Structure* 4, 581–597 (1996).
18. Dolphin, D. *The Porphyrins* (Academic Press, New York, 1978).