

## Supporting Information

### Stacking of Bacteriochlorophyll *c* Macrocycles in Chlorosome from *Chlorobium limicola* As Revealed by Intermolecular $^{13}\text{C}$ Magnetic-Dipole Correlation, X-Ray Diffraction, and Quadrupole Coupling in $^{25}\text{Mg}$ NMR

Yoshinori Kakitani<sup>‡</sup>, Yasushi Koyama<sup>‡,\*</sup>, Yuichi Shimoikeda<sup>§</sup>, Toshihito Nakai<sup>§</sup>, Hiroaki Utsumi<sup>§</sup>, Tadashi Shimizu<sup>||</sup>, and Hiroyoshi Nagae<sup>⊥</sup>

<sup>‡</sup> Faculty of Science and Technology, Kwansei Gakuin University, Gakuen, Sanda 669-1337, Japan,

<sup>§</sup> Analytical Instrument Division, JEOL Ltd., Musashino, Akishima, Tokyo 196-8558, Japan,

<sup>||</sup> National Institute for Materials Science, Sakura, Tsukuba, Ibaraki 305-0003, Japan, and

<sup>⊥</sup> Kobe City University of Foreign Studies, Gakuen-Higashimachi, Nishi-ku, Kobe 651-2187, Japan

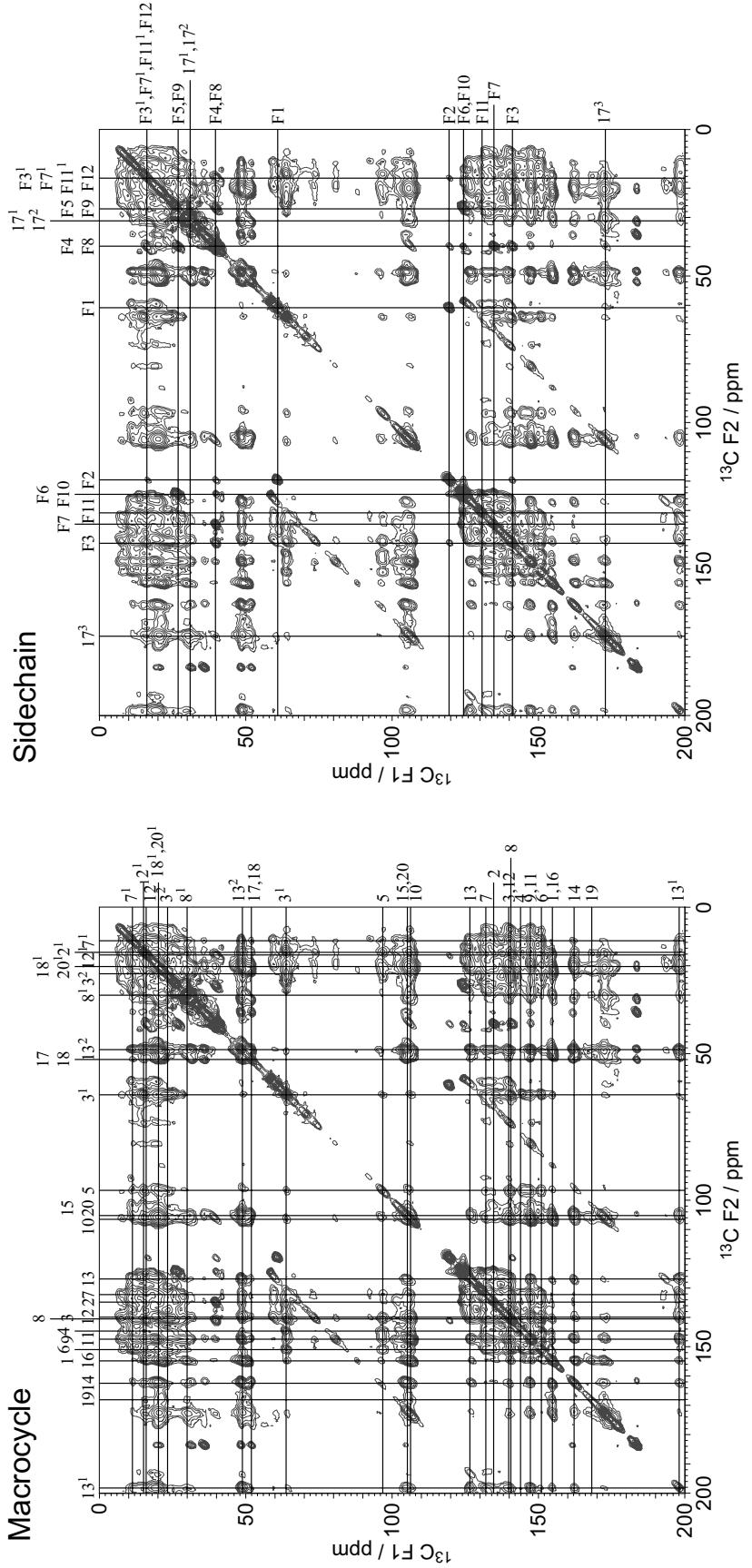


FIGURE S1: DARR spectrum of reassembled chlorosome containing 100% [ $^{13}\text{C}$ ]BChl *c* (mixing time 100ms). The assignment of correlation peaks between a pair of  $^{13}\text{C}$  magnetic dipoles are shown, along the horizontal and vertical lines as guide for eyes, by the use of the numbering of carbon atoms shown in Scheme 1 for the macrocycle (left-hand-side) and the farnesyl sidechain (right-hand-side).

***The Possibility of a Mixed Structure Consisting of (f) Weakly-Overlapped Dimers Forming***

***Displaced Layers, (a) Weakly-Overlapped Monomers Forming Structure 1 and (b)***

***Weakly-Overlapped Monomers Forming Structure 2***

One of the reviewers advised us to examine a model of mixed structure as described in the title.

The question stems from, we suppose, the fact that structure (f) implicitly contains three different stacking columns, i.e., (i) dimer-based stacking, (ii) pseudo-monomer-based stacking of structure 1-type and (iii) pseudo-monomer-based stacking of structure 2-type (see Figure 9). Then, the point is whether pseudo-monomer-based stackings of the two types, (ii) and (iii), can *partially* transform into (a) the *real* monomer-based stacking forming structure 1 and (b) the *real* monomer-based stacking forming structure 2, by rearranging the coordinations between the pair of central Mg and hydroxyethyl O atoms.

This is an extremely interesting idea, but we think this is unlikely, and difficult to prove on the present experimental basis:

(i) Generally speaking, each asymmetric unit indicated by dotted line in Figure 5 tends to take the same structure spreading in the two-dimensional lattice that is defined by the *a* and *b* axes. This is a general rule in forming a crystal structure, although there can be some disorder because the BChl *c* component consists of epimers and isomers.

(ii) Concerning the various stackings shown in Figure 5, which have been spectroscopically identified, are unique and there have been no signs of mixed stackings observed so far.

(iii) We have actually identified a *phase transformation* from the B745d-type aggregate to the

B745m-type aggregate ('d' and 'm' signify the dimer-based and monomer-based stackings) when a small amount of  $S[I,E]$  was added to the system (27). This transformation strongly supports the above idea of the homogeneously-stacked structures.

(iv) However, the set of stackings may have slightly different free energies depending on the structure of the component BChl *c* molecule, i.e., epimers *S* or *R* and isomers [E,E], [P,E] or [I,E], as well as on the solvent polarity and polarizability. Therefore, there is a possibility of transformation from one stacking to another depending on the environment.

(v) There can be a phase separation, as well, if the environmental energy is *locally* different (as the reviewer points out). Then, the system may consist of couple of *domains*. If the sizes of domains are large enough, they may be detected by X-ray diffraction most sensitively. The calculated diffraction patterns in Figure 6a–f suggest this possibility, but the diffraction patterns actually observed are too broad to detect such subtle differences.

(vi) The distribution of the carbon-to-carbon short contacts shown in Figure 3, to be compared to intermolecular  $^{13}\text{C}$  magnetic dipoles, is not be useful, because a mixed structure would predict the  $^{13}\text{C} \cdots ^{13}\text{C}$  intermolecular correlations in all over the area in the atomic number presentation. It is almost impossible to specify the three domains in the mixture.

(vii) In order to prove such mixed structures, we need to demonstrate *unique intermolecular interactions* that are present *on the surface* of a pair of domains, where the number of intermolecular interactions is expected to be much less than those in the major domains. Therefore, we need to develop some new technique to *selectively* detect such *interdomain* interactions.

(viii) Finally, we re-examined the score of agreement in our model, i.e., (f) weakly-overlapped dimers forming displaced layers (see Figure 3 and Table 2). The intermolecular  $^{13}\text{C}\cdots^{13}\text{C}$  pairs left unexplained are within a distance below 6.5 Å except for C6 $\cdots$ C7<sup>1</sup> (7.5 Å). Therefore, if we increase the limit of  $^{13}\text{C}$  magnetic-dipole interaction from 6.0 Å to 6.5 Å, the score of agreement reaches to an averaged value of 97%.

Above consideration leads us to a conclusion that such a mixed structure is unlikely and difficult to identify.