Photosynth Res (2008) 95:183–189
DOI 10.1007/s11120-007-9259-9

REGULAR PAPER

Effect of quinones on formation and properties of bacteriochlorophyll *c* aggregates

Jan Alster · Anita Zupcanova · Frantisek Vacha · Jakub Psencik

Received: 7 September 2007 / Accepted: 10 September 2007 / Published online: 9 October 2007

Abstract Chlorosomes of green photosynthetic bacterium *Chlorobium tepidum* contain aggregates of bacteriochlorophyll *c* (BChl *c*) with carotenoids and isoprenoid quinones. BChl aggregates with very similar optical properties can be prepared also in vitro either in non-polar solvents or in aqueous buffers with addition of lipids and/or carotenoids. In this work, we show that the aggregation of BChl *c* in aqueous buffer can be induced also by quinones (vitamin K_1 and K_2), provided they are non-polar due to a hydrophobic side-chain. Polar vitamin K_3, which possess the same functional group as K_1 and K_2, does not induce the aggregation. The results confirm a principal role of the hydrophobic interactions as a driving force for the aggregation of chlorosomal BChls. The chlorosomal quinones play an important role in a redox-dependent excitation quenching, which may protect the cells against damage under oxygenic conditions. We found that aggregates of BChl *c* with vitamin K_1 and K_2 exhibit an excitation quenching as well. The amplitude of the quenching depends on quinone concentration, as determined from fluorescence measurements. No lipid is necessary to induce the quenching, which therefore originates mainly from interactions of BChl *c* with quinones incorporated in the aggregate structure. In contrast, only a weak quenching was observed for dimers of BChl *c* in buffer (either with or without vitamin K_3) and also for BChl *c* aggregates prepared with a lipid (lecithin). Thus, the weak quenching seems to be a property of BChl *c* itself.

Keywords Bacteriochlorophyll aggregates · Chlorosomes · Green sulphur bacteria · Redox-dependent excitation quenching · Quinones

Abbreviations

BChl	Bacteriochlorophyll
MGDG	Monogalactosyl diglyceride

Introduction

Green photosynthetic bacteria contain a unique light-harvesting complex, the so-called chlorosome (reviews by Blankenship and Matsuura 2003; Balaban et al. 2005; Frigaard and Bryant 2006). These organelles consist mainly of bacteriochlorophyll (BChl) *c*, *d*, *e* (depending on the species). BChl *a*, carotenoids, lipids, and proteins are also present. In addition, chlorosomes contain significant amounts of isoprenoid quinones. In case of green sulphur bacteria, the main quinones are chlorobiumquinone (1′-oxomenaquinone-7) and menaquinone-7, present at total concentration of about 0.1 mol per mol BChl (Frigaard et al. 1997; Blankenship and Matsuura 2003). Chlorosomes are remarkable because their main BChl pigments are assembled into aggregates and not into pigment–protein complexes. Recent results suggest that BChls with carotenoids and quinones self-assemble into undulated lamellar nanostructures (Psencik et al. 2004; Psencik et al.

J. Alster · J. Psencik
Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

A. Zupcanova · F. Vacha
Biological Centre ASCR, Ceske Budejovice, Czech Republic

F. Vacha · J. Psencik (✉)
Institute of Physical Biology, University of South Bohemia, Nove Hrady, Czech Republic
e-mail: psencik@karlov.mff.cuni.cz

2006), rather than to hexagonally packed rod elements (5 or 10 nm diameter) proposed formerly (Staehelin et al. 1978; Staehelin et al. 1980). BChl *c*, *d* and *e* have the ability to form oligomers through the ligation of an oxygen atom in one molecule to the central magnesium in another molecule (reviews by Blankenship and Matsuura 2003; Balaban et al. 2005). The aggregation leads to strong exciton interactions between the BChls, which cause the characteristic red shift of their Q_y absorption band relatively to that of monomers. Aggregates with very similar optical properties can be prepared in vitro either in non-polar solvents (Bystrova et al. 1979; review by Tamiaki 1996) or in aqueous buffers with addition of lipids (Hirota et al. 1992; Miller et al. 1993) and/or carotenoids (Klinger et al. 2004).

Green photosynthetic bacteria comprise two distantly related groups of organisms: green sulphur and green filamentous bacteria. The green sulphur bacteria are strictly anaerobic organisms whose efficient excitation energy transfer to the reaction centre occurs only in the absence of oxygen (Frigaard and Matsuura 1999). Under aerobic conditions, the excited states of antenna pigments are rapidly quenched, both in whole cells and isolated chlorosomes (Karapetyan et al. 1980; van Dorseen et al. 1986; Wang et al. 1990; Blankenship et al. 1993; Psencik et al. 1998), by a mechanism that prevents energy transfer towards the reaction centres and charge separation therein. The reaction centres of green sulphur bacteria contain low-potential electron acceptors (iron sulphur centres), which reduce ferredoxin directly. The reduced ferredoxin may form superoxide when reacting with oxygen and consequently a variety of damaging photooxidative products (Blankenship and Matsuura 2003). The redox regulation of excitation quenching occurs at two levels: (1) within the chlorosomes, and (2) within the so-called FMO protein. The latter connects the chlorosome to cytoplasmic membrane containing the reaction centres. Quinones play a principal role in the excitation quenching within chlorosomes (Frigaard et al. 1997). In addition, oxidized BChl radicals (van Noort et al. 1997) were suggested to be involved in the quenching which occurs in the chlorosome, while tyrosine residue adjacent to BChl *a* molecule may be involved in the FMO complex (Zhou et al. 1994).

Similar excitation quenching was observed also in artificial BChl aggregates prepared from a mixture of BChls, galactolipid (monogalactosyl diglyceride, MGDG) and quinones isolated from chlorosomes. On the other hand, only a weak quenching was observed for aggregates prepared from BChls and MGDG, in the absence of quinones (Frigaard et al., 1997). Green filamentous bacteria, such as *Chloroflexus aurantiacus*, do not exhibit redox regulation of the excitation energy transfer. However, addition of certain quinones to the cell suspension causes redox-dependent quenching of the BChl *c* fluorescence similar to that observed in green sulphur bacteria (Frigaard et al. 1999).

In this work, we studied assembly of BChl *c* aggregates prepared with quinones (vitamin K_1, K_2 and K_3) and excitation quenching in these aggregates. The results show that only non-polar quinones induce both aggregation and the excitation quenching. This provides new evidence about the importance of hydrophobic interactions for the chlorosome assembly and function.

Materials and methods

Artificial aggregates were prepared using HPLC purified BChl *c* extracted from whole cells of green sulphur bacterium *Chlorobium tepidum* as described previously (Klinger et al. 2004) with following modifications. Three menadione-based quinones were tested as aggregation-inducing components: vitamin K_1 (phylloquinone, BioChemika), vitamin K_2 (menaquinone-4, Sigma) and vitamin K_3 (menadione, BioChemika). Figure 1 summarizes chemical structures of the used quinones. In addition, lipid lecithin (L-α-phosphatidylcholine, Avanti Polar Lipids) was used in control experiments instead of MGDG. BChl *c* and selected aggregation-inducing component were separately dissolved in ethanol, mixed together in required concentrations and injected vigorously into 50 mM Tris-HCl buffer of pH 8.0. The final concentration of BChl *c* in the buffer was approximately 20 μM and the concentration of organic solvents was below 1.5%. The aggregates were left for 3–5 days in darkness at room temperature to fully develop. Absorption spectra (recorded on UV/VIS Lambda12, Perkin Elmer) were used to evaluate the formation of the aggregates.

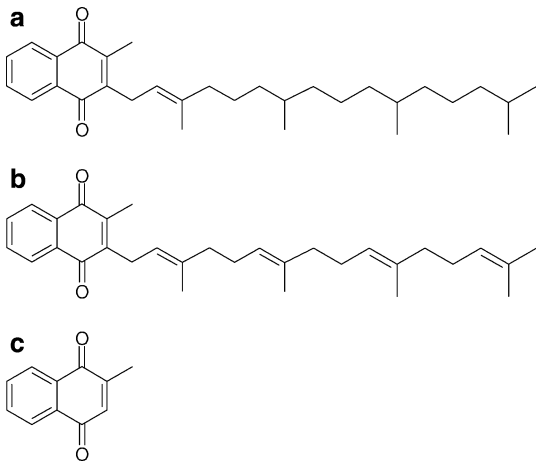

Fig. 1 Molecular structures of quinones used in this study: (**a**) vitamin K_1 (phylloquinone); (**b**) vitamin K_2 (menaquinone-4); (**c**) vitamin K_3 (menadione; 2–methyl-1,4-naphtoquinone)

The excitation quenching was examined by means of fluorescence spectroscopy. The extent of quenching was quantified by the ratio of the fluorescence intensity under reducing conditions (unquenched) to the fluorescence intensity under oxidizing conditions (quenched), denoted as a 'quenching ratio' in this work. An alternative approach based on comparing the areas under emission bands leads to the same results, within a ~5% accuracy. The quenching ratios were determined with a relative standard error not exceeding 20%. Fluorescence was excited by 460 nm laser pulses from an optical parametric oscillator (PG122, EKSPLA) which was pumped by a Q-switched Nd:YAG laser (NL303G/TH, EKSPLA). The fluorescence was detected in a right-angle geometry by means of an intensified CCD camera (PI-MAX 512RB, Roper Scientific) together with an imaging spectrometer (Triax 320, Horiba Jobin Yvon). The fluorescence spectra were averaged from 1000 accumulations and corrected for the spectral sensitivity of the experimental set-up. To achieve reducing (anaerobic) conditions, samples were incubated with ~ 20 mM sodium dithionite for about one hour before the measurement. Optical density of samples for fluorescence measurements was below 0.2 at the excitation wavelength. Absorption spectra were measured before and after the experiments to ensure no degradation occurred during the data acquisition.

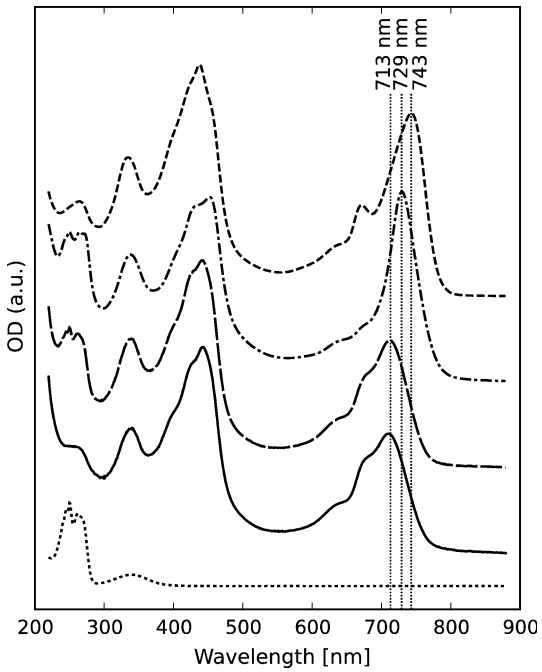

Fig. 2 Absorption spectra of BChl *c* and quinone forms in aqueous buffer: vitamin K_3 (dotted line), BChl *c* dimers (solid line), BChl *c* dimers with vitamin K_3 (molar ratio 1:1, long-dashed line), BChl *c* aggregates with vitamin K_1 (molar ratio 1:1, dash-dotted line), and BChl *c* aggregates with lecithin (molar ratio 1:1, short-dashed line). BChl *c* containing spectra were normalized at 350 nm and shifted along the intensity axis to assist visualization. Vertical lines indicate position of the main absorption maxima

Results

Aggregate formation

Pure BChl *c* is partly soluble in aqueous buffer, where it develops into a spectral form with a main Q_y absorption maximum between 710 and 715 nm (Fig. 2). This form, most probably, corresponds to an antiparallel dimer of BChl *c* (Umetsu et al. 2003; Klinger et al. 2004) and will be denoted as 'dimers' in this work.

Previously, we have observed that BChl *c* aggregates in aqueous buffers are formed not only from a mixture containing BChl *c* and lipids, but also when BChl *c* is mixed with carotenoids isolated from chlorosomes, without addition of any lipids (Klinger et al. 2004). Therefore, we were interested in finding out whether the mixture of BChl *c* with another constituent of chlorosomes, quinones, would form aggregates.

Three menadione-based quinones, which do not naturally occur in chlorosomes, were used: vitamins K_1 and K_2, non-polar, possessing a hydrophobic chain and vitamin K_3, a polar molecule without the chain (Fig. 1). The latter is well soluble in the aqueous buffer with characteristic absorption maxima at ~250 and ~265 nm (Fig. 2). Such an absorption spectrum is also typical for the other two vitamins (not shown), however, they are not well soluble in water. An injection of BChl *c* mixed with either vitamin K_1 or K_2 into aqueous buffer led to formation of aggregates (Fig. 2). The spectral shift of the Q_y band above the wavelengths typical for BChl *c* dimers became apparent at the quinone to BChl *c* molar ratio between 0.1:1 and 0.2:1. The aggregates of BChl *c* with vitamin K_1 achieved maximal red shift of their Q_y absorption band (738 nm) at molar ratio 1.3:1. The development of aggregates induced by vitamin K_2 was very similar, although the red shift was slightly smaller (734 nm). Both positions of absorption maxima fall into the range typical for BChl *c* oligomers. Interestingly enough, further increase of the quinone concentrations led to a slight blue shift of the Q_y absorption band. The presence of the quinones in the sample was discernible by their characteristic absorption between 230 and 260 nm.

In contrast to non-polar vitamins K_1 and K_2, polar vitamin K_3 apparently did not induce BChl *c* aggregation. Instead, absorption spectrum consisted of contributions from dissolved quinones and BChl *c* dimers (Fig. 2). Absorption maximum of the Q_y band was around 713 nm for all tested vitamin K_3 concentrations, i.e. up to molar ratio 2:1, vitamin K_3 to BChl *c*.

To compare the aggregation and quenching ability of aggregates formed with and without quinones, we also prepared aggregates from a mixture of BChl *c* and a lipid lecithin, which was shown to induce aggregation of synthetic zinc chlorins (Miyatake et al. 1999) and BChl *e* (Steensgaard et al. 2000). Measured absorption spectra of BChl *c*-lecithin samples revealed presence of BChl aggregates at the molar ratio of 0.5:1 (lecithin to BChl *c*) and higher. The dimer was the prevailing form for smaller concentrations of lecithin. The maximal red shift of the BChl *c* Q_y absorption band (746 nm), achieved at the molar ratio of 1.5:1, is larger than that observed for aggregates with quinones. It is worth mentioning that absorption of a monomer-like form of BChl *c* (670 nm) was observed together with aggregates, increasingly prominent with higher lecithin concentration. This absorption arises, most probably, from isolated BChls embedded in lecithin micelles.

Fluorescence quenching

Figure 3 summarizes fluorescence spectra of BChl *c* in aqueous buffer, either pure or mixed with a quinone or lipid in a molar ratio of 1:1. Fluorescence spectra of BChl *c* dimers, both with and without vitamin K_3, are very similar. Surprisingly, the emission maxima are exceedingly red shifted (maximum at ~755 nm) relatively to Q_y absorption (maximum at ~710 nm). BChl *c* aggregates, with lecithin, vitamin K_1 or K_2, show emission maxima at ~770–780 nm, depending on characteristics of the Q_y band of BChl *c*.

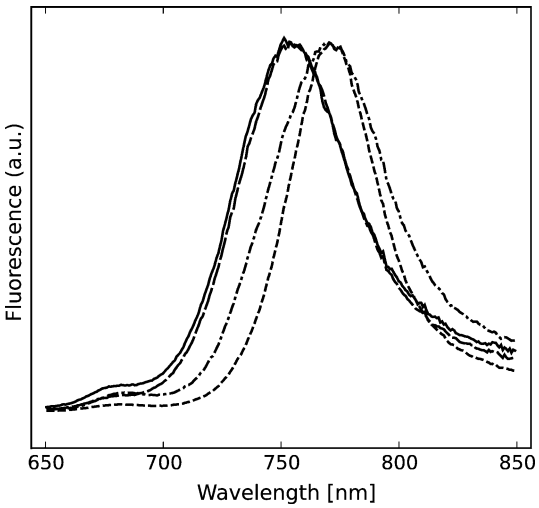

Fig. 3 Fluorescence spectra of BChl *c* forms in aqueous buffer under reducing conditions: BChl *c* dimers (solid line), BChl *c* dimers with vitamin K_3 (molar ratio 1:1, long-dashed line), BChl *c* aggregates with vitamin K_1 (molar ratio 1:1, dash-dotted line), and BChl *c* aggregates with lecithin (molar ratio 1:1, short-dashed line). Fluorescence spectra were normalized to their maxima

All studied samples exhibited a redox-dependent quenching of fluorescence, however, with a significantly different extent. The BChl *c* dimers exhibited only a weak redox-dependent fluorescence quenching. The quenching ratio was 1.5 (see Materials and Methods for a definition of the 'quenching ratio' used in this work). The aggregates of BChl *c* with lecithin exhibited also a weak fluorescence quenching of 1.5 regardless of lecithin concentration (Fig. 4). Significantly stronger quenching ratio was observed for the BChl *c* aggregates with vitamins K_1 or K_2. At low quinone concentrations (molar ratio below 0.1:1, quinone to BChl *c*), when BChl *c* dimer was still the prevailing form, the quenching ratio was approximately 3 for both K_1 and K_2 and then approximately linearly increased with the quinone concentration (Fig. 4). For the range of quinone concentrations 0.3:1–2:1 (BChl *c* was in aggregated form), the quenching ratio reached a plateau around the value of 7. However, the ratio increased again for higher concentration of quinones and was as high as 35 at the molar ratio of 17:1, the highest tested value (Fig. 4, inset). The dimers of BChl *c* prepared with vitamins K_3 displayed average quenching ratio of 1.6, comparable with pure BChl *c* dimers. The slight increase of quenching ratio with a vitamin K_3 concentration (1.9 at molar ratio 2:1, vitamin K_3 to BChl *c*), that was observed, may not be significant considering the experimental error.

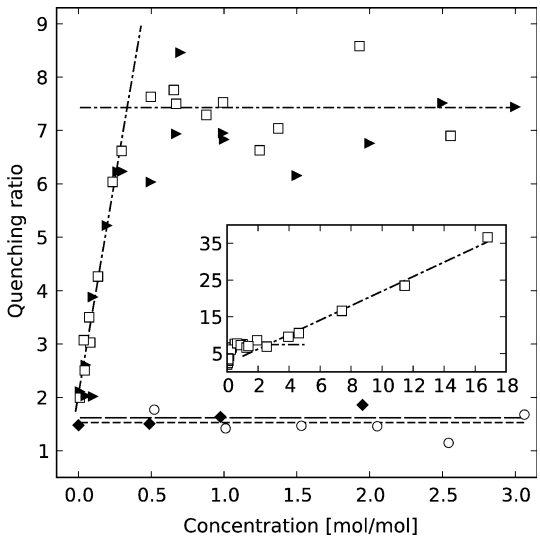

Fig. 4 The ratio of the fluorescence intensity under reducing conditions to fluorescence intensity under oxidizing conditions (quenching ratio) of BChl *c* forms as a function of concentration of aggregation-inducing component or vitamin K_3 (molar ratio, admixture to BChl *c*) used in the aggregates preparation. The admixtures were lecithin (circles, short-dashed line), vitamin K_1 (squares, dash-dotted line), vitamin K_2 (triangles), and vitamin K_3 (diamonds, long-dashed line). The inset shows the quenching ratio for wider range of vitamin K_1 concentrations. The eye-guiding lines underline the concentration ranges of approximately constant and linearly increasing quenching ratios

Discussion

In this work, we have shown that menadione-based quinones are able to induce BChl *c* aggregation in aqueous environment provided they possess a hydrophobic tail. Both phytyl (vitamin K_1) and farnesyl (vitamin K_2) exhibit this ability. It is worth noting that menaquinone-7, which naturally occurs in chlorosomes, differs from vitamin K_2 only in the length of the non-polar chain, having it longer by three isoprene units. This makes menaquinone-7 more hydrophobic than vitamin K_2. The polarity of quinone obviously plays the fundamental role in its aptitude of stimulating aggregate formation. The polarity of the molecule increases and quinone loses its ability to induce BChl *c* aggregation by complete removal of the hydrophobic chain, as observed for vitamin K_3 (menadione). The results suggest that suitable non-polar molecules can induce the aggregate formation in polar environments by augmentation of the hydrophobic interactions between esterifying alcohols. This is in agreement with a previously suggested hypothesis that the hydrophobic interactions are the main driving forces for the aggregate formation in polar environment (Klinger et al. 2004). In addition, the non-polar tail probably helps to anchor these quinones in the hydrophobic space between the undulated BChl aggregates in the lamellar complex. In conclusion, aggregates can be obtained from a mixture of BChl with any of the major components of the chlorosome (carotenoids, non-polar quinones, and lipids).

The molar ratio of quinone to BChl *c* necessary for induction of the full red shift of the Q_y absorption band is higher than quinone concentration found in chlorosomes (approx. 0.1:1). However, lipids (and carotenoids) present in chlorosomes certainly contribute to the aggregation process. It should be noted that molar ratios reported in this work were determined for initial mixtures. It is very likely that a portion of the non-polar quinone molecules was not incorporated into the BChl *c* aggregates. This is supported by the fact that addition of quinones leads to additional scattering background in absorption spectra, which is probably due to large clusters of quinones without BChl *c*. Similar scattering can be observed for the solution/emulsion of the vitamin K_1 and K_2 in the buffer.

Fluorescence spectra of aggregates prepared from BChl *c* and quinones are very similar to those reported by Frigaard et al. (1997) for aggregates of BChl *c*, MGDG, and quinones. To our knowledge, fluorescence spectra of BChl *c* dimers were not reported previously. A surprising feature is the extremely large Stokes shift between absorption and fluorescence maximum ($\sim$40 nm), reaching values typical for BChl aggregates. This indicates a close proximity of dimers in aqueous buffers, which allows for efficient downhill excitation transfer between neighbours within inhomogeneously broadened distribution of dimers. The tendency of dimers to cluster together is a result of their hydrophobic nature and can be also observed as a precipitation (flake formation) under higher concentrations or after prolonged storage.

Our results confirm a previous observation of weak fluorescence quenching for BChl *c* aggregates with lipids. We observed the quenching ratio of 1.5 for the BChl *c* aggregates with lecithin, which is somewhat weaker than the quenching ratio of 3 reported by Frigaard et al. (1997) for BChl *c* aggregates with MGDG. In addition, we also determined quenching ratio of 1.5 for BChl *c* dimers. The agreement between the value obtained for BChl *c* dimers and aggregates with lecithin supports the idea that this weak quenching is a property of BChls and is induced neither by lipids nor by aggregation.

Nevertheless, the main contribution to the quenching in chlorosomes arises certainly from the BChl-quinone interactions. Aggregates of BChl *c* with quinones exhibit a considerable redox-dependent fluorescence quenching, which amplitude depends on concentration of quinones. At natural quinone concentration (0.1:1, quinone to BChl *c*), the fluorescence quenching is smaller ($\sim$3) than that for aggregates of BChl *c* with MGDG and the same concentration of menaquione-7 (quenching ratio 5.8) reported by Frigaard et al. (1997). This discrepancy can be explained by the presence of MGDG, which ensured that BChl *c* was in the aggregated form already for these small (natural) quinone concentrations. However, BChl *c* dimer was still the prevailing form in our sample at these quinone concentrations and the excitation quenching could not be as effective as in aggregates with a significant initial excitation delocalization and fast exciton relaxation. The quenching ratio increases with concentration of quinones, as a result of quinone incorporation into the structure of the formed aggregates. For quinone concentrations sufficient to induce fully developed aggregates, the quenching ratio reaches a stable value around 7, similar to values reported for BChl *c*-MGDG aggregates with chlorosomal quinones menaquione-7 or chlorobiumquinone (quenching ratio 6.9) reported by Frigaard et al. (1997). For molar ratios larger than 2.5:1 (quinone to BChl *c*), a further increase of the quenching ratio was observed. Thus, the complete concentration dependence obviously does not follow a linear Stern–Volmer relationship. The maximal quenching ratio observed in this work was 35 (for quinone concentration 17:1), which is comparable with the extensive quenching observed in the chlorosome (quenching ratio of 10–40, Frigaard et al. 1997, 1998). An important conclusion from these results is that quinone mediated quenching does not require lipid presence.

Polar vitamin K_3 does not induce redox-dependent fluorescence quenching, although it contains the same

functional group as vitamins K_1 and K_2. This implies that a close interaction between BChls and quinones in the aggregates is necessary for efficient quenching of BChl *c* fluorescence by quinones. In the lamellar model, isoprenoid quinones occupy the hydrophobic space between the undulated planes of BChl aggregates, which ensure such an interaction. Polar quinones cannot participate in the hydrophobic interactions, which explains why they did not induce either aggregate formation or fluorescence quenching in our study. However, Frigaard et al. (1999) observed redox-dependent quenching of the fluorescence from BChl *c* aggregates in whole cells of *Chloroflexus aurantiacus* after addition of polar quinones into suspension. Our results do not provide an insight into the mechanism showing how polar quinones incorporate into the chlorosomes. Another puzzling evidence is the fact that chlorosomes of *Chloroflexus aurantiacus* do not exhibit the fluorescence quenching at aerobic conditions although they contain menaquinone-10 in an amount similar to the total amount of quinones in *Chlorobium tepidum* (Frigaard et al. 1997). This is striking because similar menaquinone-7 was shown to be only moderately weaker fluorescence quencher than chlorobiumquinone in aggregates prepared from BChl *c* and MGDG at pH 7.0 (see above, Frigaard et al. 1997). The midpoint potentials of the quinones seem to be the crucial parameters for understanding different extent of fluorescence quenching in chlorosomes from various bacteria (Frigaard and Bryant 2006).

In conclusion, our results provide new evidence about an important role of hydrophobic interactions for the chlorosome assembly and function. We have shown that, in addition to lipids and carotenoids, non-polar quinones are also able to induce aggregation of BChl *c* in an aqueous environment, while polar quinones do not. Incorporation of the non-polar quinones into the aggregate structure is a necessary prerequisite for an efficient fluorescence quenching under aerobic conditions.

Acknowledgements This research was funded by Czech Ministry of Education, Youth and Sports (contracts MSM0021620835, MSM6007665808 and AV0Z50510513), and Czech Science Foundation (contracts 202/05/H003 to J.A. and 206/05/2739 to J.P.). We thank Dr. Juan B. Arellano for valuable discussions and Alena Vackova and Jessica Arab for proofreading of our manuscript.

References

Balaban TS, Tamiaki H, Holzwarth AR (2005) Chlorins programmed for self-assembly. Top Curr Chem 258:1–38

Blankenship RE, Cheng P, Causgrove TP, Brune DC, Wang SH, Chon J, Wang J (1993) Redox regulation of energy transfer efficiency in antennas of green photosynthetic bacteria. Photochem Photobiol 57:103–107

Blankenship RE, Matsuura K (2003) Antenna complexes from green photosynthetic bacteria. In: Green BR, Parson WW (eds) Light-harvesting antennas. Kluwer Academic Publishers, Dordrecht, pp 195–217

Bystrova MI, Mal'gosheva IN, Krasnovsky AA (1979) Study of molecular mechanism of self-assembly of aggregated forms of bacteriochlorophyll *c*. Mol Biol 13:440–451

Frigaard NU, Takaichi S, Hirota M, Shimada K, Matsuura K (1997) Quinones in chlorosomes of green sulfur bacteria and their role in the redox-dependent fluorescence studied in chlorosome-like bacteriochlorophyll *c* aggregates. Arch Microbiol 167:343–349

Frigaard NU, Matsuura K, Hirota M, Miller M, Cox RP (1998) Studies of the location and function of isoprenoid quinones in chlorosomes from green sulfur bacteria. Photosynth Res 58:81–90

Frigaard NU, Matsuura K (1999) Oxygen uncouples light absorption by the chlorosome antenna and photosynthetic electron transfer in the green sulfur bacterium *Chlorobium tepidum*. BBA-Bioenergetics 1412:108–117

Frigaard NU, Tokita S, Matsuura K (1999) Exogenous quinones inhibit photosynthetic electron transfer in *Chloroflexus aurantiacus* by specific quenching of the excited bacteriochlorophyll *c* antenna. BBA-Bioenergetics 1413:108–116

Frigaard NU, Bryant DA (2006) Chlorosomes: antenna organelles in photosynthetic green bacteria. In: Shively JM (eds) Complex Intracellular Structures in Prokaryotes (series: Microbiology Monographs, vol. 2). Springer, Berlin, pp 79–114

Hirota M, Moriyama T, Shimada K, Miller M, Olson JM, Matsuura K (1992) High degree of organization of bacteriochlorophyll *c* in chlorosome-like aggregates spontaneously assembled in aqueous solution. Biochim Biophys Acta 1099:271–274

Karapetyan NV, Swarthoff T, Rijgersberg CP, Amesz J (1980) Fluorescence emission spectra of cells and subcellular preparations of a green photosynthetic bacterium. Effects of dithionite on the intensity of the emission bands. Biochim Biophys Acta 593:254–260

Klinger P, Arellano JB, Vacha FE, Hala J, Psencik J (2004) Effect of carotenoids and monogalactosyl diglyceride on bacteriochlorophyll c aggregates in aqueous buffer: Implications for the self-assembly of chlorosomes. Photochem Photobiol 80:572–578

Miller M, Gillbro T, Olson JM (1993) Aqueous aggregates of bacteriochlorophyll *c* as a model for pigment organization in chlorosomes. Photochem Photobiol 57:98–102

Miyatake T, Tamiaki H, Holzwarth AR, Schaffner K (1999) Self-assembly of synthetic zinc chlorins in aqueous microheterogeneous media to an artificial supramolecular light- harvesting device. Helvetica Chimica Acta 82:797–810

Psencik J, Polivka T, Nemec P, Dian J, Kudrna J, Maly P, Hala J (1998) Fast energy transfer and exciton dynamics in chlorosomes of the green sulfur bacterium Chlorobium tepidum. J Phys Chem A 102:4392–4398

Psencik J, Ikonen TP, Laurinmaki P, Merckel MC, Butcher SJ, Serimaa RE, Tuma R (2004) Lamellar organization of pigments in chlorosomes, the light harvesting complexes of green photosynthetic bacteria. Biophys J 87:1165–1172

Psencik J, Arellano JB, Ikonen TP, Borrego CM, Laurinmaki PA, Butcher SJ, Serimaa RE, Tuma R (2006) Internal structure of chlorosomes from brown-colored Chlorobium species and the role of carotenoids in their assembly. Biophys J 91:1433–1440

Staehelin LA, Golecki JR, Fuller RC, Drews G (1978) Visualization of the supramolecular architecture of chlorosome (Chlorobium type vesicles) in freeze-fractured cells of *Chloroflexus aurantiacus*. Arch Microbiol 119:269–277

Staehelin LA, Golecki JR, Drews G (1980) Supramolecular organization of chlorosome (Chlorobium vesicles) and of their membrane attachment site in *Chlorobium limicola*. Biochim Biophys Acta 589:30–45

Steensgaard DB, Wackerbarth H, Hildebrandt P, Holzwarth AR (2000) Diastereoselective control of bacteriochlorophyll e aggregation. 3(1)-S-BChl e is essential for the formation of chlorosome-like aggregates. J Phys Chem B 104:10379–10386

Tamiaki H (1996) Supramolecular structure in extramembraneous antennae of green photosynthetic bacteria. Coord Chem Rev 148:183–197

Umetsu M, Seki R, Kadota T, Wang ZY, Adschiri T, Nozawa T (2003) Dynamic exchange properties of the antiparallel bacteriochlorophyll *c* dimers. J Phys Chem B 107:9876–9882

van Dorssen RJ, Gerola PD, Olson JM, Amesz J (1986) Optical and structural properties of chlorosomes of the photosynthetic green sulfur bacterium Chlorobium limicola. Biochim Biophys Acta 848:77–82

van Noort PI, Zhu Y, LoBrutto R, Blankenship RE (1997) Redox effects on the excited-state lifetime in chlorosomes and bacteriochlorophyll *c* oligomers. Biophys J 72: 316–325

Wang J, Brune DC, Blankenship RE (1990) Effects of oxidants and reductants on the efficiency of excitation transfer in green photosynthetic bacteria. Biochim Biophys Acta 1015:457–463

Zhou W, LoBrutto R, Lin S, Blankenship RE (1994) Redox effects on the bacteriochlorophyll-*a* containing Fenna-Matthews-Olson protein from Chlorobium tepidum. Photosynth Res 41:89–96