

Femtosecond Probe of Structural Analogies Between Chlorosomes and Bacteriochlorophyll *c* Aggregates

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ABSTRACT Bacteriochlorophyll *c* pigments extracted from light-harvesting chlorosomes in green photosynthetic bacteria are known to self-assemble into aggregates whose electronic spectroscopy resembles that of intact chlorosomes. Femtosecond optical experiments reveal that the chlorosomes and their reconstituted aggregates exhibit closely analogous internal energy transfer kinetics and exciton state evolution. These comparisons furnish compelling new evidence that proteins do not exert a major local role in the BChl *c* antenna pigment organization of intact chlorosomes.

Chlorosomes are ellipsoidal light-harvesting bodies ($100 \times 30 \times 12$ nm) that are appressed to the inside of the cytoplasmic membrane in green photosynthetic bacteria (Staelin et al., 1978; Olson, 1980; Blankenship et al., 1995). The $\sim 10^4$ antenna chromophores in a chlorosome are predominantly bacteriochlorophyll (BChl) *c*, *d*, or *e* pigments, which are responsible for an intense, broad Q_y electronic absorption band between 720 and 750 nm. Electronic excitations arising from light absorption in the BChl *c/d/e* antenna in the interior of the chlorosome are sharply funneled into a smaller, 790–800 nm BChl *a* antenna ($\sim 10^2$ pigments), which serves as a baseplate assembly that interfaces the light-harvesting pigments to the reaction centers in the cytoplasmic membrane (Betti et al., 1982; Gerola and Olson, 1986).

The vast majority of photosynthetic antennae are pigment–protein complexes, in which the pigment organization, electronic couplings, and energy transfer pathways are dictated by tertiary protein structure (Schirmer et al., 1985; Tronrud et al., 1986; Krauss et al., 1993; Kühlbrandt et al., 1994). Biochemical and spectroscopic evidence suggests that BChl *c/d/e* antennae in chlorosomes consist instead of pigment oligomers, in which pigment–pigment rather than pigment–protein interactions dominate the supramolecular structure (Krasnovsky and Bystrava, 1980; Smith et al., 1983; Olson et al., 1985; Brune et al., 1987; Holzwarth et al., 1990; Hirota et al., 1992). Extraction of chlorosomes from *Chlorobium limicola* (Hirota et al., 1992) or *Chloroflexus aurantiacus* (Miller et al., 1993) yields a protein-free phase containing BChl *c*, BChl *a*, carotenoids, and lipids. Dilution of this extract in methanol with aqueous buffer causes spontaneous self-assembly of the BChl *c* pigments into large aggregates, encapsulated in lipid mi-

celles 80–100 nm in diameter. Whereas the Q_y absorption band of monomeric BChl *c* in organic solvents typically appears at ~ 670 nm, the reconstituted BChl *c* aggregates exhibit red-shifted absorption and fluorescence spectra that nearly coincide with those of intact BChl *c* antennae in chlorosomes. They also exhibit similar linear dichroism (Hirota et al., 1992), circular dichroism (Miller et al., 1993), and resonance Raman spectra (Lutz and van Brakel, 1988; Nozawa et al., 1990; Feiler et al., 1994; Hildebrandt et al., 1994). This suggests that the aggregates and chlorosomes show analogous collinearity, helicity, and pigment interactions. The 5.7-, 11-, and 18-kDa proteins characteristic of chlorosomes in *C. aurantiacus* have not been detected in the SDS-PAGE of the corresponding aggregate (Miller et al., 1993; Griebenow and Holzwarth, 1989). Nevertheless, the function of BChl *c*-binding proteins in chlorosomes has remained a subject of spirited controversy (Eckhardt et al., 1990; Wullink et al., 1991; Hildebrandt et al., 1991; Niedermeier et al., 1992).

Few comparisons have been drawn between the energy transfer functions in chlorosomes and aggregates, because many of the internal BChl *c/d/e* processes are complete within ≤ 1 –2 ps (van Noort et al., 1994; Savikhin et al., 1994). Optical pump–probe experiments that used 40–80-fs FWHM light pulses from a self-mode-locked Ti:sapphire laser (Savikhin et al., 1994; Savikhin and Struve, 1994a) have enabled us to contrast the earliest events in intact chlorosomes and in reconstituted BChl *c*-lipid aggregates from the green sulfur bacterium *Chlorobium tepidum*. Fig. 1 shows time-dependent absorption difference signals for chlorosomes and aggregates excited with laser pulses at 749 nm, near the BChl *c* Q_y absorption band maximum. In these one-color experiments, the sample absorbance is probed at variable time delay by light pulses that are spectrally and temporally identical to the pump pulses ($\Delta\lambda \sim 8$ nm, $\Delta t \sim 70$ fs). The absorption transients $\Delta A_{\parallel}(t)$ and $\Delta A_{\perp}(t)$ were obtained by use of probe pulses polarized parallel and perpendicular, respectively, to the pump polarization. The signals in Fig. 1 are negative-going, because the absorption difference at this wavelength is dominated throughout by BChl *c* ground-state photobleaching (PB) and Q_y stimulated emission (SE). This figure also shows the derived anisot-

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Abbreviations used: BChl, bacteriochlorophyll; ESA, excited-state absorption; PB, photobleaching; SE, stimulated emission.

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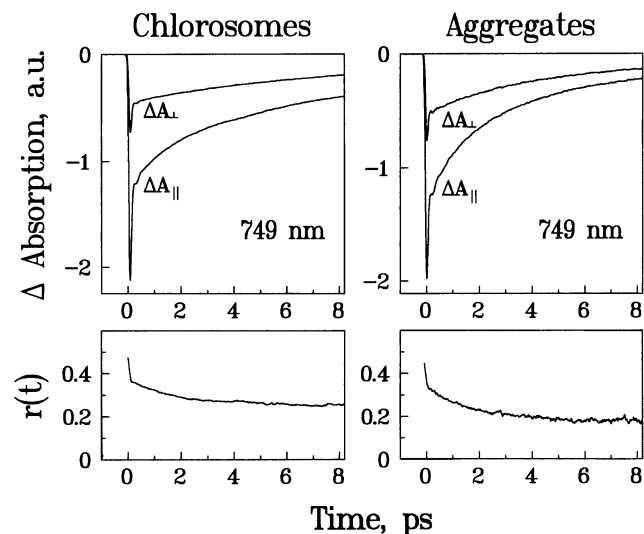


FIGURE 1 Time-resolved absorption difference signals $\Delta A_{\parallel}(t)$ and $\Delta A_{\perp}(t)$, obtained with probe pulses polarized parallel and perpendicular to the pump polarization, for intact chlorosomes from the green bacterium *Chlorobium tepidum* (left) and their reconstructed BChl *c* aggregates (right). The pump and probe pulse spectra are centered at 749 nm, with 8-nm bandwidth; the instrument function (laser autocorrelation) is 110 fs FWHM. Lower panels show the derived anisotropy functions $r(t)$. Negative-going ΔA signals correspond to photobleaching and stimulated emission. Nonzero anisotropies r_{∞} at long times indicate that the domain of BChl *c* pigments over which the electronic excitation equilibrates is not random, but exhibits considerable order.

ropy functions $r(t) = (\Delta A_{\parallel}(t) - \Delta A_{\perp}(t)) / (\Delta A_{\parallel}(t) + 2\Delta A_{\perp}(t))$, which contain information about dynamic changes in light absorption polarization that are due to energy transfers among differently oriented BChl *c* pigments. Optimized fits of the single-exponential model function $r(t) = (r_0 - r_{\infty})\exp(-t/\tau) + r_{\infty}$ to the experimental curves yield similar anisotropy decay times in both cases ($\tau = 1.8$ ps and 1.9 ps for the intact chlorosomes and aggregates, respectively). The aggregates exhibit a smaller residual anisotropy at this wavelength ($r_{\infty} = 0.18$, versus 0.25 in chlorosomes). In other one-color experiments for BChl *c* absorption wavelengths between 720 and 770 nm (not shown), the aggregates and chlorosomes (Savikhin et al., 1995) exhibit similar anisotropy decay times τ , but the aggregates show systematically lower r_{∞} . The residual anisotropy depends weakly on wavelength in the main BChl *c* absorption region; the ranges of r_{∞} are 0.19–0.25 in the chlorosomes and 0.17–0.20 in the aggregates. This suggests that, although the kinetics of electronic energy transfers between contrastingly oriented BChl *c* chromophores in the aggregates closely mimic those in intact chlorosomes, the mean pigment organization is somewhat more disordered in the aggregates.

One-color isotropic absorption difference signals $\Delta A(t) = \Delta A_{\parallel}(t) + 2\Delta A_{\perp}(t)$ are shown in Fig. 2 in an 8-ps time window for pump–probe wavelengths near 760 nm. They reflect on the excited-state population decay kinetics for the BChl *c* species that absorb at the probe wavelength. For a

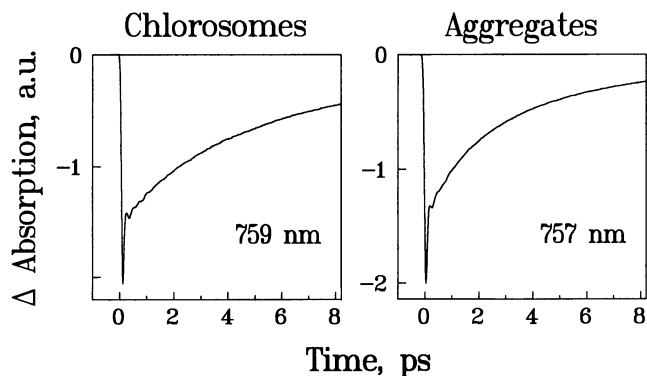


FIGURE 2 Isotropic absorption difference signals $\Delta A(t)$, obtained with probe pulses polarized at the magic angle (54.7°) from the pump polarization, for intact chlorosomes (left) and BChl *c*-lipid aggregates (right). The pump and probe pulse spectra are centered at 759 nm for the chlorosomes and at 757 nm for the aggregates, with 9-nm bandwidth. The instrument functions are 93 and 107 fs FWHM, respectively. Biexponential analyses of the profiles in this 8-ps time window yield the lifetime components 2.3 and 9.6 ps for the chlorosomes and 1.7 and 7.0 ps for the aggregates. These analyses overlook the femtosecond oscillations observed at very early times (cf. Fig. 4).

given excitation wavelength, the signals observed in the two samples are comparable in magnitude. Biexponential fits to these profiles yield PB/SE decay components with lifetimes of 2.3 ps (34%) and 9.6 ps (66%) for the chlorosomes and 1.7 ps (48%) and 7.0 ps (52%) for the aggregates. These profiles typify the fact that for most pump–probe wavelengths ≥ 749 nm, the lifetime families 1–3 and 5–10 ps are recurring motifs (with similarly large preexponential factors) in the BChl *c* PB/SE decays of both intact chlorosomes (Savikhin et al., 1995) and reconstituted aggregates. They underscore the correspondence between the picosecond energy transfer kinetics in the two systems. A major difference in the isotropic kinetics occurs at the longer BChl *c* wavelengths (770–790 nm), where a 30–40-ps PB/SE decay component (attributable to energy transfers from the oligomeric BChl *c* antenna to the BChl *a*-protein baseplate antenna complex) gains importance in intact chlorosomes (Savikhin et al., 1995). No analogous BChl *c* \rightarrow BChl *a* energy transfer component is found in the protein-free aggregates, because BChl *a* pigments are not incorporated into the BChl *c*-lipid aggregates. The rapid BChl *c* excitation decay in the aggregates (Fig. 2) likely stems from the incorporation of redox-active defect sites during self-assembly, because addition of sodium dithionite greatly increases the BChl *c* fluorescence yield in similar aggregates (Miller et al., 1993). Hence, the overall PB/SE decay in aggregates probably reflects the time scale of excitation diffusion to randomly situated quenching sites. In the present experiments, a 740-nm laser pulse typically excites 1 of every $\sim 10^3$ BChl *c* pigments (i.e. ~ 10 pigments per chlorosome in the experiments on intact chlorosomes). In separate experiments, we have used laser powers low enough to excite 1 of every ~ 30 chlorosomes (not shown). The annihilation-free decays still exhibit 1–2- and 5–15-ps lifetime compo-

nents, so that these lifetimes are characteristic of BChl *c* energy transfers in the intact chlorosomes under low-light illumination. However, the distribution of amplitudes between these lifetime components (as yielded by biexponential fits) gravitates toward the faster component as the laser power is increased.

Like intact chlorosomes from *C. tepidum* (Savikhin et al., 1995), the reconstituted aggregates exhibit coherent oscillations in their one-color isotropic BChl *c* PB/SE profiles at very early times (Fig. 3). The oscillations are damped within 1–2 ps, which is comparable with one of the energy transfer time scales observed in the isotropic and anisotropic decays. However, this is longer than the time scales of subpicosecond events observed in *C. tepidum* (Savikhin et al., 1995); some of the nuclear modes responsible for the coherences may be delocalized low-frequency modes. Fourier analyses of the oscillating parts of these profiles yield similar dominant frequency components (albeit with different weightings) in the neighborhood of 90 and 130 cm^{-1} . Undue emphasis should not be placed on this correspondence, because the Fourier analyses rely on arbitrary fitting criteria for the monotonic parts of the isotropic decays. However, these spectra resemble each other far more closely than they resemble the Fourier spectra of coherent oscillations observed in chlorosomes from the green thermophilic bacterium *C. aurantiacus* (Savikhin et al., 1994), whose oligo-

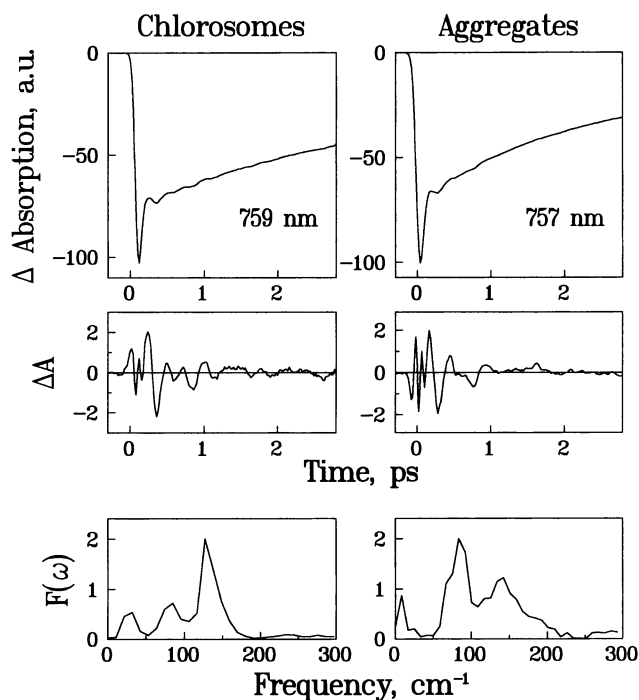


FIGURE 3 Coherent oscillations in isotropic absorption difference signals from chlorosomes (*left*) and aggregates (*right*) at very early times. The respective pump–probe pulse spectra are centered at 759 and 757 nm. Laser spectrum and autocorrelation widths are 9 nm and 93 fs for the chlorosomes and 9 nm and 107 fs for the aggregates. The oscillating parts of $\Delta A(t)$ and their Fourier-transform spectra are shown in the center and lower panels.

meric antenna comprises a mixture of BChl *c* homologs that is different from the one found in *C. tepidum* (Brune et al., 1987). Vibrational coherences may be signatures of environmental effects on low-frequency mode couplings and coherence times. Although they are not observed for BChl *a* monomers in solution (Savikhin and Struve, 1994b), they appear in the pump–probe spectroscopy of the LH1 BChl *a* antenna in *Rhodobacter sphaeroides* (Chachisvilis et al., 1994) and of the BChl *a* special pair in bacterial reaction centers (Vos et al., 1993). Our coherences may originate from pigment–pigment bonding modes in aggregates; if so, Fig. 3 suggests that the intact BChl *c* oligomer structure resembles that in the protein-free aggregates.

Two-color isotropic profiles are compared in Fig. 4 for chlorosomes and aggregates excited near 760 nm. In both cases, the mean probe wavelength is 20–25 nm to the blue of the pump wavelength. Their details of PB/SE rise behavior are intriguingly similar. In both cases, a prompt excited-state absorption (ESA) signal is superseded within 10–20 fs by a PB/SE signal. A slower PB rise feature follows, with 4.2- and 1.2-ps kinetics for chlorosomes and aggregates, respectively. Earlier pump–probe experiments on intact chlorosomes from *C. tepidum* (Savikhin et al., 1995) have shown that their BChl *c* antenna kinetics exhibit more spectral heterogeneity than those of chlorosomes from *C. aurantiacus* (Savikhin et al., 1994). Broadband absorption difference experiments confirm that the picosecond rise kinetics in the two-color profile for chlorosomes from *C. tepidum* stem from uphill spectral equilibration among inequivalent BChl *c* chromophores, following 760-nm excitation at the red edge of the 740-nm absorption band (Savikhin et al., 1995). Similar uphill equilibration occurs in the aggregates (Fig. 4). Two-color profiles of BChl *c* aggregates excited at 740 nm and probed 40 nm to the red (not shown) show marked 100–200-fs PB/SE rise features, arising from downhill spectral equilibration.

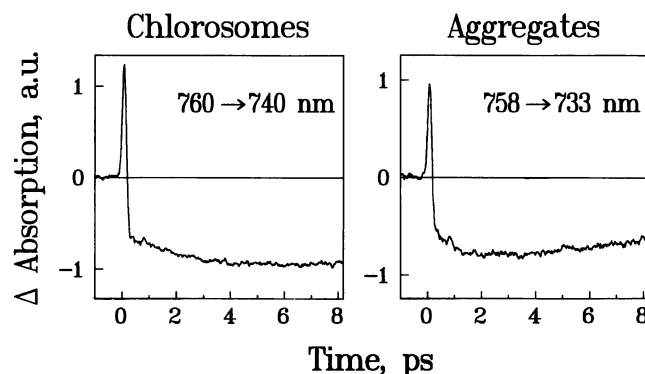


FIGURE 4 Two-color isotropic absorption difference signals for chlorosomes (*left*) and aggregates (*right*), probed at 20 to 25 nm to the blue of the excitation wavelength. For the chlorosomes, the excitation and probe pulse spectra are centered at 760 and 740 nm, with 6–7-nm bandwidth and 179-fs FWHM cross-correlation; for the aggregates, they are centered at 758 and 733 nm, with 171-fs FWHM cross-correlation. Both BChl *c* assemblies exhibit 10–20-fs switching from prompt ESA to PB/SE, followed by picosecond PB/SE rise kinetics.

The ultrafast ESA \rightarrow PB/SE switching in Fig. 4 is of particular interest, because its kinetics require a PB/SE rise component with 10–20-fs lifetime for simulation. It cannot be a coherent coupling artifact (Cong et al., 1993), because there is no spectral overlap between the 6–7-nm bandwidth pump and probe pulses in these two-color experiments. Such rapid transients are not observed for BChl *a* monomers in solution (Savikhin and Struve, 1994b) or for BChl *a*-protein antenna complexes (FMO trimers) from *C. tepidum* (Savikhin and Struve, 1994a). However, ESA \rightarrow PB/SE switching has been observed with similar kinetics in uphill two-color experiments on chlorosomes from *C. aurantiacus* (Savikhin et al., 1994). Fig. 5, which gives absorption difference spectra at several time delays for intact chlorosomes excited at 760 nm, shows that the BChl *c* PB/SE spectrum is localized near the excitation wavelength for at \sim 20 fs. The empirical hole broadens during the first few tens of femtoseconds, evolving by 200 fs into a PB/SE spectrum with a bandwidth similar to that of the absorption contour of the BChl *c* antenna (Savikhin et al., 1994; Savikhin et al., 1995). The origin of this hole broadening is uncertain. In an antenna with pigment–pigment couplings V , coherent energy transfer (through electronic wave-packet

propagation) is projected to occur on a time scale $t \sim (4cV)^{-1}$, where c is the speed of light (Förster, 1965). Although the couplings are of the order of 100 cm^{-1} in pigment–protein complexes such as FMO trimers (Pearlstein, 1992), the 1400 cm^{-1} spectral shift between the 740-nm BChl *c* Q_y absorption band in chlorosomes and the 670-nm absorption band of BChl *c* monomers in methanol suggests that V is as high as $\sim 700 \text{ cm}^{-1}$ in chlorosomes (Brune et al., 1987). The coherent energy transfer times are correspondingly expected to be ~ 80 and ~ 10 fs in FMO trimers and chlorosomes. Fig. 5 suggests that the prompt absorption difference spectrum excited at 760 nm is dominated by a BChl *c* PB/SE hole near the excitation wavelength. However, two-color experiments that used 780-nm excitation (not shown) indicate that the prompt spectrum does not simply shift with the pump wavelength; its shape varies considerably with pump wavelength. Our results thus do not support the hypothesis that the prompt spectrum generally resembles the difference spectrum of a single BChl *c* species that absorbs near the pump wavelength. The ~ 40 -nm bandwidth of the BChl *c* steady-state absorption spectrum is of the same order of magnitude as the lifetime broadening expected for 20–40-fs events.

In summary, the reconstituted BChl *c*-lipid aggregates reproduce many of the internal energy transfer functions of the intact BChl *c* antenna in chlorosomes from *C. tepidum*, on time scales ranging from ~ 10 ps down to ~ 10 fs. The energy transfer kinetics are sensitive to the pigment organization through its effects on the exciton couplings and (in the incoherent excitation hopping limit) on the Förster transition probabilities. Our results suggest that the local pigment organizations in the two systems are very similar, because they exhibit similar kinetics in their isotropic and anisotropic absorption difference profiles, similar coherent oscillations, similar effects of spectral heterogeneity in their two-color profiles, and similar photobleaching evolution during the first few femtoseconds. In this strongly coupled antenna, the slower events (such as the 1–2-ps anisotropy decays) almost certainly represent not single-step energy transfers between BChl *c* pigments but instead cumulative or long-range energy transfers that span many pigments. The residual anisotropies r_∞ thus depend on the long-range ordering of BChl *c* pigments, which on the average is less pronounced in the aggregates than in the chlorosomes.

Finally, although proteins do not appear to influence the local pigment organization in the BChl *c* antennae of intact chlorosomes, our experiments do not rule out the possibility that proteins are instrumental in positioning the BChl *c* antenna for efficient energy transfers into the BChl *a*-protein baseplate antenna.

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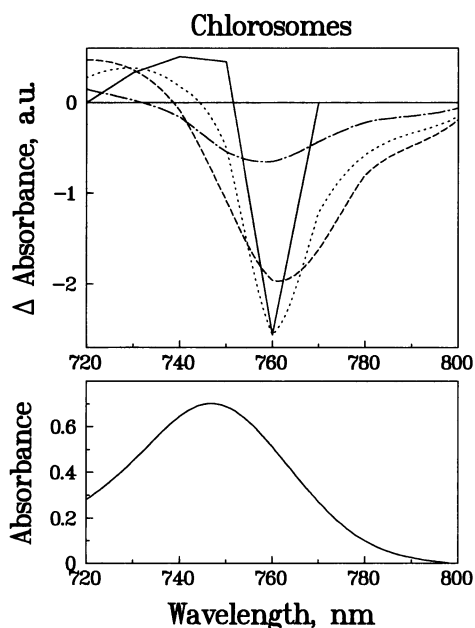


FIGURE (Top) Absorption difference spectra for intact chlorosomes, assembled from two-color profiles obtained under 760-nm excitation by probe wavelengths at ~ 10 nm-intervals from 720 to 800 nm. Time delays are 20 fs (solid curve), 50 fs (dotted curve), 200 fs (dashed curve), and 8 ps (dotted-dashed curve). The horizontal axis is the probe wavelength; the vertical axis is the absorption difference signal at all time delays except 20 fs. In the latter case, the vertical axis corresponds to the amplitude of the 20-fs component derived from best fits of triexponential model functions to the two-color profiles. Although the coherent coupling artifact may contribute to the 760-nm PB/SE signal at the earliest times, it is essentially absent in the two-color experiments performed with probe wavelengths ≤ 750 nm or ≥ 770 nm. (Bottom) The steady-state chlorosome absorption spectrum.

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