THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

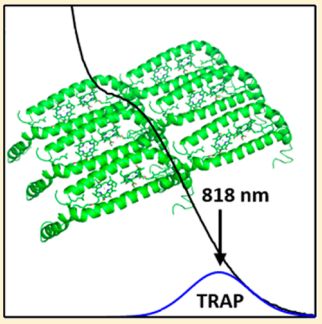
Alternative Excitonic Structure in the Baseplate (BChl *a*–CsmA Complex) of the Chlorosome from *Chlorobaculum tepidum*

Adam Kell,[†] Jinhai Chen,[†] Mahboobe Jassas,[†] Joseph Kuo-Hsiang Tang,[‡] and Ryszard Jankowiak*[,†,§]

[†]Department of Chemistry and [§]Department of Physics, Kansas State University, Manhattan, Kansas 66506, United States

[‡]Department of Chemistry and Biochemistry, Clark University, Worcester, Massachusetts 01610, United States

ABSTRACT: In the photosynthetic green sulfur bacterium *Chlorobaculum tepidum*, the baseplate mediates excitation energy transfer from the light-harvesting chlorosome to the Fenna–Matthews–Olson (FMO) complex and subsequently toward the reaction center (RC). Literature data suggest that the baseplate is a 2D lattice of BChl *a*–CsmA dimers. However, recently, it has been proposed, using 2D electronic spectroscopy (2DES) at 77 K, that at least four excitonically coupled BChl *a* are in close contact within the baseplate structure [Dostál, J.; et al., *J. Phys. Chem. Lett.* **2014**, *5*, 1743]. This finding is tested via hole burning (HB) spectroscopy (5 K). Our results indicate that the four excitonic states identified by 2DES likely correspond to contamination of the baseplate with the FMO antenna and possibly the RC. In contrast, HB reveals a different excitonic structure of the baseplate chromophores, where excitation is transferred to a localized trap state near 818 nm via exciton hopping, which leads to emission near 826 nm.



Green Sulfur Bacteria. Green sulfur bacteria (GSB), which possess complete photosynthetic machinery, are anoxygenic phototrophs that thrive in an oxygen-free, sulfur-rich environment and can live in extremely low light ecosystems, for example, at depths of 100 m in the Black Sea[1] or in volcanic vents in the absence of solar radiation.[2] GSB contain unique antennas known as chlorosomes,[3,4] which differ from other antenna complexes by their large size (ellipsoidal bodies with a length varying from 100 to 200 nm, width of 50–100 nm, and height of 15–30 nm[5]). Additionally, the bacteriochlorophylls (BChls) (up to 250 000) are reversibly self-assembled[6] with no supporting protein matrix, constituting a unique system among all classes of natural photosynthetic complexes. These properties make GSB very attractive as a model for biomimetic solar energy collection devices[7−12] and excitation energy transfer (EET) studies.

In addition, GSB contain a BChl *a* protein called the Fenna–Matthew–Olson (FMO) complex.[13,14] Between the chlorosomes and FMO complexes is the baseplate, that is, oligomeric BChl *a*–CsmA (see Figure 1). FMO connects the chlorosome–baseplate system to the reaction center (RC) and functionally forms a bridge to transfer the excitation energy to the RC for charge separation.[15] Each chlorosome is suggested to interact with approximately 150–300 FMO trimers and 25–40 RCs.[16] The organization of CsmA proteins as a 2D crystalline lattice was directly observed via electron cryomicroscopy,[3] and the structure of the CsmA protein has been determined by liquid-state NMR.[17] However, the exact arrangement of the CsmA units in the baseplate, including relative orientation and distances between *individual* BChl *a* molecules, and the strength of interaction with BChl *c* are not known.[9,18,19] Interactions between chlorosome pigments (BChl *c*) and BChl *a* of the baseplate were recently studied theoretically and are believed to be weak, with only a minor

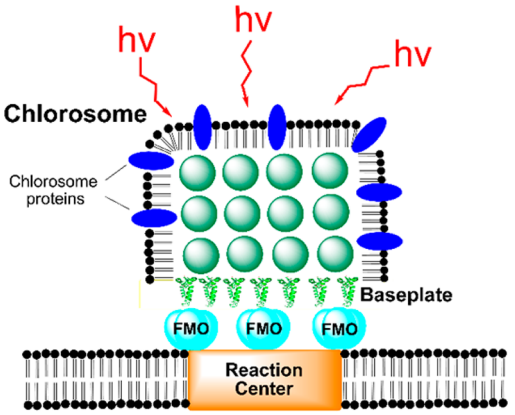


Figure 1. Schematic structural model for GSB.[11]

effect on baseplate transition energies.[20] The BChl *a* of the baseplate absorbs at about 796 nm and is not aggregated like the BChl *c* molecules. Stoichiometric measurements strongly indicate that in *Chlorobaculum* (*Cb.*) *tepidum*, one CsmA protein binds a single BChl *a* molecule,[9,21] and the presence of a single histidine residue (His25) supports this conclusion.[17,22] A detailed structure of the baseplate is not known, although several models of the BChl *a*–CsmA dimer have been proposed.[22−24] Interestingly, while the BChl dipole–dipole angles (30–125°) and center-to-center distances (7–18 Å) vary significantly in these models, the calculated dipole couplings (assuming $|\mu| = 6.1$ D) are in the range of 30–35 cm^{-1}. Further studies of photosystems of various complexities

Received: May 22, 2015
Accepted: June 23, 2015
Published: June 23, 2015

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702–2707

(i.e., chlorosome−baseplate, chlorosome−baseplate−FMO, and chlorosome−baseplate−FMO−RC) are of great interest and should shed more light on chlorosome−baseplate interactions as well as electronic structure and EET dynamics of the BChl *a*−CsmA system.

The chlorosome−baseplate photosynthetic system is of great interest because it is likely that it represents one of the earliest antenna systems. Despite the dynamical disorder effects on the electronic transitions of the BChl *c*, previous simulations showed that the exciton delocalizes over the entire aggregate (a single BChl *c* "roll") in 100−200 fs,[24,25] and intrachlorosomal EET in the tubular antenna elements toward the baseplate is extremely fast, that is, less than 500 fs.[20] Experimentally, femtosecond pump−probe has also revealed energy equilibration on a 50−100 fs time scale for both *Cb. tepidum* and *Chloroflexus* (*Cf.*) *aurantiacus*.[26,27] A two-color, femtosecond transient absorption study also suggested very fast intrachlorosomal EET in the time range of 117−270 fs.[28] In the same study,[28] it was shown that excitation of the blue side of the BChl *c* Q_y absorption band (685 nm) while probing at 807 nm (where both the antenna elements and the baseplate absorb) leads to a fast transient absorption anisotropy decay component of about 1 ps for the chlorosomes of *Cb. tepidum*, *Prosthecochloris* (*P.*) *aestuarii*, and *Cf. aurantiacus*. The time constant of ∼1 ps was proposed to reflect both intrachlorosomal EET from the initially excited state to lower-lying local states and EET between BChl *a* molecules of the baseplate. The longer anisotropy components of 6.6 (*Cf. aurantiacus*), 8.8 (*P. aestuarii*), and 12.1 ps (*Cb. tepidum*) were assigned to chlorosome to baseplate energy transfer.[28] In summary, the reported times of EET from the chlorosome to the baseplate are on a picosecond time scale, for example, 6−12 ps,[28] although longer time constants of 5−20,[20] 12−40,[29] 30−40,[30] and 280 ps[31] were also proposed to correspond to EET from the chlorosome to the baseplate pigments.

Excitonic Structure of Baseplate BChl a. Very recently, it has been suggested that the organization of baseplate BChl *a* is more complex than previously indicated,[32] being comprised of a BChl *a* multimer. That is, it was proposed that 2D electronic spectroscopy (2DES) at 77 K revealed spectroscopic features typical of an excitonic system of at least four coupled BChl *a*. In this work, we examine the electronic/excitonic structure of baseplate chromophores focusing on sample purity as a small contamination by FMO and RC complexes could lead to a more complex excitonic structure. We also address the EET dynamics between BChl *c* → BChl *a* and BChl *a* → BChl *a* via highly selective spectroscopic techniques, that is, resonant and nonresonant hole burning (HB) spectroscopy, to provide more insight into the relationship between excitonic structure, function, and dynamics of the chlorosome−baseplate system. It is anticipated that a better understanding of excitonic structure and EET pathway(s) between BChl *a* in the 2D paracrystalline lattice of CsmA proteins could inspire future designs of more efficient light-harvesting devices.[22]

Low-Temperature Absorption and Emission Spectra. Figure 2A shows two 5 K absorption spectra (normalized at 756 nm) obtained for two chlorosome−baseplate samples of different purities (see curves a and b). Although absorption spectra in Figure 2A are similar to those reported in the literature,[32] our high-resolution, low-temperature spectra a and b differ in the 790−830 nm baseplate transition region, suggesting that curve b is slightly contaminated by FMO (and possibly RC) complexes (vide infra). Frame B shows emission spectra from

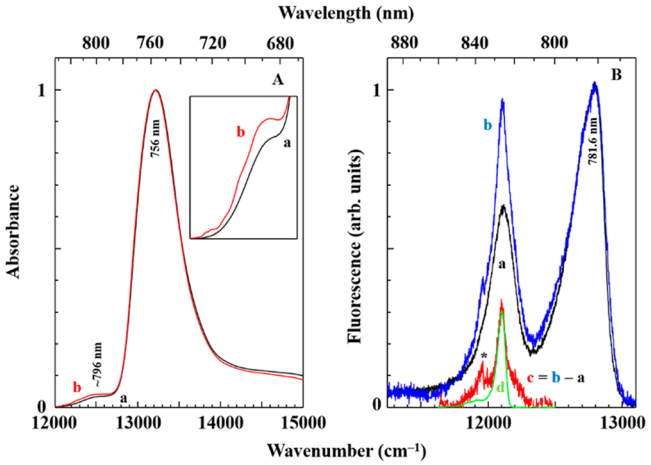


Figure 2. (A) Normalized low-temperature (5 K) absorption spectra obtained for two chlorosome−baseplate samples. Curve a represents the absorption of the chlorosome−baseplate, while curve b shows that the corresponding sample had slight contamination of FMO/RC antenna. The inset shows the 11800−12800 cm^{-1} region. (B) Emission spectra obtained for chlorosome−baseplate (curve a) and chlorosome−baseplate−FMO−RC (curve b) samples, with main bands at 781.6 and 825.7 nm corresponding to the chlorosome and baseplate emission, respectively. Spectrum c = b − a. Spectrum d (green curve) is the 5 K emission from intact, isolated FMO complexes.[33]

chlorosome−baseplate and chlorosome−baseplate−FMO−RC samples, with main bands at 781.6 (BChl *c*) and 825.7 nm (BChl *a*).

Hole-Burned Spectra. The low-energy part of the 5 K absorption spectrum of the chlorosome−baseplate is shown by curve a in Figure 3A. Spectrum b is the nonresonant (persistent), nonphotochemical HB spectrum (λ_B = 488.0 nm). The HB spectrum was obtained with a fluence (f) of approximately 2100 J/cm^2, where $f = I \cdot t_B$, with I and t_B corresponding to the laser intensity and burn time, respectively. The hole shape is fit by a Gaussian (black curve) with position at 12 200 cm^{-1} (818.3 nm) and a fwhm of 240 cm^{-1}. Spectrum

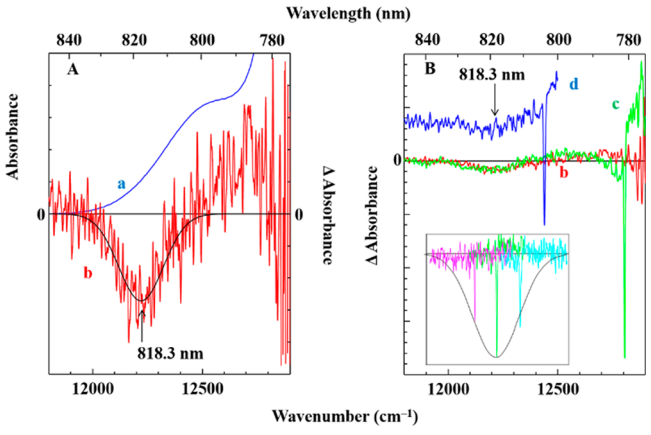


Figure 3. (A) Spectra a and b are the 5 K absorption and HB spectra (λ_B = 488.0 nm; $f \approx$ 2100 J/cm^2) obtained for the chlorosome−baseplate. (B) Spectrum b from frame A is replotted and compared to HB spectra obtained for λ_B = 781.0 (green curve c) and 804.0 nm (blue curve d, offset for clarity). All spectra reveal the lowest-energy trap state at 818.3 nm. The inset in frame B shows the ZPA spectrum burned in the lowest-energy state of the baseplate.

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702−2707

b from frame A is replotted in frame B for comparison with HB spectra obtained for two other excitation wavelengths, that is, λ_B = 781.0 (curve c) and 804.0 nm (curve d). All spectra reveal just one broad low-energy trap state at 818.3 nm. Spectra c and d also show the zero-phonon holes (ZPHs) at λ_B with fwhms (corrected for spectral resolution) of 3.6 and 5.3 cm^{-1}, respectively. Recall that the width of the ZPH in resonant HB spectra depends on the lifetime of the excited state and the "pure" dephasing and/or EET time (τ_{EET}).[34] Note that λ_B = 781.0 nm lies with the low-energy exciton state of the BChl *c* aggregate,[30] that is, at this wavelength, chlorosome BChl *c* molecules are excited resonantly. Such a low-energy state for chlorosomes was clearly observed in the zero-phonon action (ZPA) spectrum[30] and 2DES data (real part) for chlorosomes from *Cb. tepidum*.[32] The ZPA spectrum (obtained for constant *f*) for the low-energy state of the baseplate is shown in the inset of frame B. The widths of the three ZPHs are resolution-limited. Interestingly, the envelope of the ZPA spectrum is similar to the Gaussian fit of the lowest-energy trap near 818.3 nm.

Curves a in Figure 4 are 5 K absorption spectra, while curves b−e correspond to *f*-dependent, nonresonant HB spectra

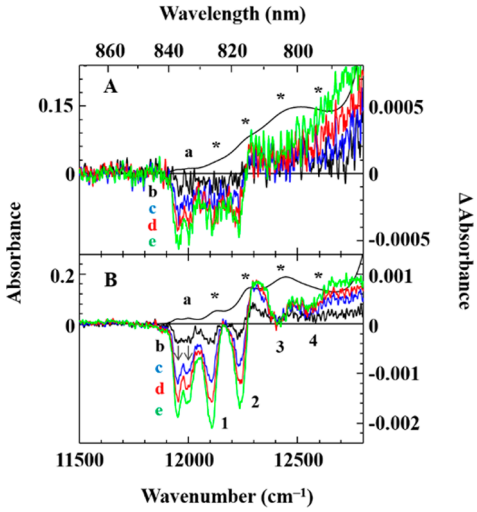


Figure 4. (A) Chlorosome−baseplate sample with a small amount of FMO−RC. (B) Chlorosome−baseplate sample with a large amount of FMO−RC. Curves a are 5 K absorption spectra, while curves b−e correspond to *f*-dependent, nonresonant HB spectra (λ_B = 488.0 nm). $f \approx$ 20, 230, 860 and 2100 J/cm^2 for holes b−e, respectively. Asterisks mark the energetic positions of states determined from 77 K 2DES data,[32] with holes labeled 1−4 indicating similar states in 5 K HB spectra. The two gray arrows mark bleaches of the lowest-energy state of the RC antenna.

obtained with λ_B = 488.0 nm. Frames A and B show spectra for chlorosome−baseplate samples with increasing amounts of FMO and RC antenna, respectively. On the basis of previous study of isolated FMO complexes,[33] holes labeled 1−3 (located near 827, 818, and 806 nm) were also observed in FMO complexes. The weak feature near 797 nm may result from bleach of the RC antenna pigment as both frames of Figure 4 show RC contamination. The asterisks label the four very similar electronic transitions resolved in 77 K time evolution spectra, which were previously assigned to the baseplate[32] (vide infra).

On Pure Chlorosome−Baseplate Systems. Extensive studies of multiple samples revealed that only spectra in Figure 2 (curves a) correspond to pure absorption and emission of the chlorosome−baseplate system that is free of detectable FMO/RC contamination (vide infra). The fluorescence difference spectrum in Figure 2B (i.e., curve c = b − a) clearly shows a narrow emission band at 826.4 nm that is identical to the fluorescence spectrum measured for isolated (intact) FMO complexes[33] (see green curve d), indicating that spectrum b is contaminated with FMO. The weak narrow emission band in curve c, labeled by an asterisk, corresponds to the previously mentioned minor contamination from the RC. Comparison of emission spectra obtained for various chlorosome−baseplate samples revealed that samples are often contaminated by FMO or FMO/RC complexes, while the emission spectrum of the chlorosome−baseplate−FMO−RC is always similar to spectra measured for whole cells.[30,35]

We note that we could not burn any resonant holes in the vicinity of the chlorosome (BChl *c*) absorption band maximum (756 nm). This is consistent with various time domain spectroscopic data, which showed that exciton relaxation in chlorosomes occurs on a very fast time scale, that is, 100−200 fs.[26−28] That is, femtosecond relaxation competes with the HB process, leading to an extremely small HB quantum yield at these frequencies. The ZPH at 781.0 nm in Figure 3B (curve c) is fitted with a Lorentzian profile and corrected for spectral resolution, where the fwhm (Γ_{hole} = 3.6 cm^{-1}) corresponds to a homogeneous line width (Γ_{hom}) of 1.8 cm^{-1}. (Note that $\Gamma_{hole} = 2\Gamma_{hom}$).[34,36] This shows that τ_{EET} from BChl *c* → BChl *a* is ∼3 ps, in agreement with literature data.[30] This value was obtained from eq 1

$$\Gamma_{hom}(cm^{-1}) = \frac{1}{2\pi c T_1} + \frac{1}{\pi c T_2^*} + \frac{1}{2\pi c \tau_{EET}} \approx \frac{1}{2\pi c \tau_{EET}} \quad (1)$$

where T_1 is the fluorescence lifetime, T_2^* is the "pure" dephasing time (which at 5 K is very large in comparison to T_1), and *c* is the speed of light in cm/s.[34] Interestingly, selective excitation at λ_B = 804.0 nm (curve d) also shows a ZPH that, after correction for spectral resolution, gives Γ_{hom} = 2.7 cm^{-1}. This suggests that there is likely uncorrelated EET from the baseplate BChl *a* absorbing at energies > ∼12400 cm^{-1} to low-energy BChl *a*, that is, energy cascading down the energy ladder in agreement with the observed low-energy trap at 818.3 nm (12220 cm^{-1}, fwhm = 240 ± 30 cm^{-1}). Thus, we propose that baseplate emission originates from the tail states of the density of states (DOS), where the exciton dwell time exceeds its intrinsic lifetime. The estimated τ_{EET} from high-energy BChl *a* to the low-energy BChl *a* within the baseplate absorption band is about 2 ps. HB spectra imply that excitation ends up in the baseplate states near 818.3 nm, meaning that energy is efficiently transferred to a localized state that leads to the observed emission near 826 nm (see Figure 2B). Of course, in chlorosome−baseplate−FMO systems, energy would be further transferred into the lowest-energy state(s) of FMO and subsequently to the RC. We show below that minor contamination(s), if present, while not resolved in absorption at 77 K and/or room temperature, may still drastically change interpretation of the excitonic structure and dynamics of BChl *a* molecules constituting the baseplate.

Nature of Excitonic States Observed in Chlorosome−Baseplate Systems Contaminated with FMO and RC. To address the differences in the electronic structure of baseplate chromophores observed in this work and ref 32, we present in Figure 4 low-temperature (5 K) absorption and *f*-dependent, non-

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702−2707

resonant HB spectra obtained for two chlorosome−baseplate samples, which contain amounts of FMO and RC contributions (vide supra). The holes observed near 827, 818, and 806 nm most likely correspond to FMO excitonic states.[33] We hasten to add that the FMO bands are slightly shifted in comparison with isolated FMO because they are superimposed on the baseplate absorption band and weak RC absorption in the same spectral region, complicating any interpretation of their electronic/excitonic structure. While the weak feature near 797 nm may result from bleach of high-energy FMO pigments, it could also be ascribed to RC antenna pigments as both frames of Figure 4 show RC contamination. The presence of the RC antenna pigments is consistent with the observation of the two holes near 834 and 837 nm (see arrows in Figure 4B), which are known to correspond to the low-energy states of the RC antenna pigments.[37,38] The P840 band is not observed in these spectra due to partial photo-oxidation of the special pair, whose contribution has been revealed by redox chemistry (to be reported elsewhere). Because the data for the pure chlorosome−baseplate system (shown in Figure 3) show drastically different behavior and spectra shown in Figure 4 are in very good agreement with 2DES data,[32] we suggest that the four electronic transitions reported in ref 32 should not be assigned to baseplate pigments but to the excitonic states of BChl *a* residing within the FMO/RC antenna. Thus, the assignment (indicated via asterisks) of the 77 K energy states located near 12590 (794 nm), 12420 (805 nm), 12260 (815 nm), and 12120 cm^{-1} (825 nm)[32] to the BChl *a* baseplate, in light of the data shown above, is most likely incorrect. Note that the bands labeled 1−4 are slightly red-shifted compared to 2DES data due to lower temperature (5 versus 77 K) and different spectral resolutions used (4 versus 50 cm^{-1}).

Baseplate Structure. The baseplate structure seems to be less complex than proposed in ref 32. Our data support an arrangement of weakly coupled dimers, as reported in refs 22, 23, and 24, and exciton hopping along the 2D network of CsmA dimers to the low-energy trap at 818.3 nm, which emits at 825.7 nm. Thus, our data are consistent with the model reported in ref 22 that baseplate CsmA proteins arranged as a 2D paracrystalline lattice[3] bind one BChl *a* per CsmA protein, while EET can be understood in terms of a random walk on an energetically disordered network, where the excitation can move coherently within the DOS distribution of site energies.[39,40] Thus, an electronic excitation could visit many sites via hopping (i.e., downhill jumps) and "freeze" at the energetically broad low-energy trap that is most likely located at the interface between the baseplate and FMO proteins. A qualitative description of energy relaxation in systems with large energetic disorder and a random walk on the 2D surface of the baseplate BChl *a* molecules is beyond the scope of this Letter, and it remains to be established whether the Anderson−Mott transition could be invoked to explain the origin of the low-energy trap. This could have important implications regarding efficiency of EET from the baseplate pigments to the FMO complexes.

From the data reported in this work, there is excellent spectral overlap between the emission of baseplate pigments and low-energy exciton states of FMO expected for an efficient Förster-type EET from the baseplate to the FMO complex, which in turn (in intact GSB) further transfers energy to the RC for charge separation.[15] While detailed structural information is not available, a distance of 15 Å between the baseplate and FMO was estimated in recent theoretical calculations.[24] Nevertheless, if FMO complexes are present in the chlorosome−baseplate system, excitation energy is efficiently transferred to FMO, decreasing the bleach of baseplate pigments, in agreement with the shapes of HB spectra (see Figure 4). Finally, we note that data obtained for intact, isolated FMO samples[33] are in perfect agreement with data presented in this work. For example, the maximum of the FMO fluorescence band (826.4 nm)[33] fits well the fluorescence difference curve shown in Figure 2B, confirming one of our conclusions in ref 33, that absorption and fluorescence spectra reported in the literature (often measured for different FMO samples) were slightly blue-shifted due to purification/isolation procedures and/or destabilization effects.

Concluding Remarks. It has been shown that the low-energy trap of baseplate pigments spans the same energy range as FMO pigments (from about 12000 to 12400 cm^{-1}), that is, the baseplate pigments are well coupled to the two lowest-energy states of FMO. This in turn suggests that energy harvested by baseplate pigments can be efficiently transferred to FMO within the 2D lattice. The low-energy trap in the baseplate at 818.3 nm is most likely formed via exciton hopping, and HB data are consistent with dimers of CsmA proteins containing two BChl *a* molecules sandwiched between the hydrophobic regions and bound near the histidine.[22,23] In summary, our results indicate the following: (i) nonresonant and resonant HB spectra obtained at 5 K for the pure chlorosome−baseplate system question the recent suggestion that at least four BChl *a* are in close contact within the baseplate protein;[32] (ii) there is a large static diagonal disorder of baseplate BChl *a* (absorption bandwidth $\approx$ 625 cm^{-1}) with a localized trap state at 818.3 nm (fwhm $\approx$ 240 cm^{-1}) that leads to emission at 825.7 nm; and (iii) the four excitonic states identified at 77 K via 2DES[32] most likely correspond to contamination of the baseplate with the FMO antenna and possibly the RC. Finally, HB spectra show that EET from the chlorosome BChl *c* → BChl *a* of the baseplate and BChl *a* → BChl *a* (within the baseplate) occur in 2.9 ± 0.1 and 2.0 ± 0.1 ps, respectively, indicating that the baseplate receives the exciton quickly, rapidly directing it to the lowest-energy baseplate trap (with a maximum at 818.3 nm), which releases the exciton to the FMO complexes.

■ EXPERIMENTAL METHODS

The *Cb. tepidum* cultures grown at 45 °C were harvested at the steady-state growth. The membrane fraction was obtained through ultracentrifugation at 48 000 rpm for 2 h. The chlorosome was extracted from membrane fractions using 2 NaI in 20 mM tris-HCl followed by sucrose gradient separation via ultracentrifugation at 28 000 rpm for 16 h, which gave a concentrated top layer and less concentrated middle layer. The top layer contained more concentrated and pure chlorosomes (i.e., the chlorosome−baseplate complex), and the middle layer contained chlorosome with contamination of other antenna complexes. For HB experiments, samples were diluted with 50:50 (v/v) buffer/glass solution. The glass-forming solution was 55:45 (v/v) glycerol/ethylene glycol.

Details about the measurement setup were described elsewhere.[41] Here, only a brief description is given. A Bruker HR125 Fourier transform spectrometer was used to measure the absorption and HB spectra with resolutions of 4 and 2−4 cm^{-1}, respectively. The fluorescence spectra were collected by a Princeton Instruments (PI) Acton SP-3200 spectrograph equipped with a back-illuminated CCD camera (PI Action Spec10, 1340 × 400) with a resolution of 0.1 nm. The laser

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702−2707

source for both nonresonant HB and fluorescence was 488.0 nm, produced from a Coherent Innova 200 argon ion laser, and tunable wavelengths came from a Coherent CR899 Ti:sapphire laser (line width 0.07 cm^{-1}) pumped by a Spectra-Physics Millenia Xs diode laser (532 nm). Laser power in the experiments was precisely set by a continuously adjustable neutral density filter. All experiments were performed at 5 and 77 K inside of an Oxford Instruments Optistat CF2 cryostat with sample temperature read and controlled by a Mercury iTC temperature controller.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ryszard@ksu.edu. Address: Department of Chemistry, 213 Chemistry/Biochemistry Building, Kansas State University, Manhattan, KS 66506, U.S.A. Phone: +001 785 532-6785. Fax: +001 785 532-6666.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-SC0006678 (to R.J.). J.K.T. was supported by start-up funds from Clark University and thanks group members for assisting in sample preparation.

REFERENCES

(1) Manske, A. K.; Glaeser, J.; Kuypers, M. M. M.; Overmann, J. Physiology and Phylogeny of Green Sulfur Bacteria Forming a Monospecific Phototrophic Assemblage at a Depth of 100 Meters in the Black Sea. *Appl. Environ. Microbiol.* **2005**, *71*, 8049−8060.

(2) Beatty, J. T.; Overmann, J.; Lince, M. T.; Manske, A. K.; Lang, A. S.; Blankenship, R. E.; van Dover, C. L.; Martinson, T. A.; Plumley, F. G. An Obligately Photosynthetic Bacterial Anaerobe from a Deep-Sea Hydrothermal Vent. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 9306−9310.

(3) Oostergetel, G. T.; van Amerongen, H.; Boekema, E. J. The Chlorosome: A Prototype for Efficient Light Harvesting in Photosynthesis. *Photosynth. Res.* **2010**, *104*, 245−255.

(4) Orf, G. S.; Blankenship, R. E. Chlorosome Antenna Complexes from Photosynthetic Bacteria. *Photosynth. Res.* **2013**, *116*, 315−331.

(5) Martinez-Planells, A.; Arellano, J. B.; Borrego, C. M.; López-Iglesias, C.; Gich, F.; Garcia-Gil, J. Determination of the Topography and Biometry of Chlorosomes by Atomic Force Microscopy. *Photosynth. Res.* **2002**, *71*, 83−90.

(6) Balaban, T. S.; Tamiaki, H.; Holzwarth, A. R. Chlorins Programmed for Self-Assembly. *Top. Curr. Chem.* **2005**, *258*, 1−38.

(7) Balaban, T. S.; Holzwarth, A. R.; Schaffner, K.; Boender, G.-J.; de Groot, H. J. M. CP-MAS ^{13}C-NMR Dipolar Correlation Spectroscopy of ^{13}C-Enriched Chlorosomes and Isolated Bacteriochlorophyll *c* Aggregates of *Chlorobium tepidum*: The Self-Organization of Pigments Is the Main Structural Feature of Chlorosomes. *Biochemistry* **1995**, *34*, 15259−15266.

(8) Miyatake, T.; Tamiaki, H.; Holzwarth, A. R.; Schaffner, K. Self-Assembly of Synthetic Zinc Chlorins in Aqueous Microheterogeneous Media to an Artificial Supramolecular Light-Harvesting Device. *Helv. Chim. Acta* **1999**, *82*, 797−810.

(9) Sakuragi, Y.; Frigaard, N.-U.; Shimada, K.; Matsuura, K. Association of Bacteriochlorophyll *a* with the CsmA Protein in Chlorosomes of the Photosynthetic Green Filamentous Bacterium *Chloroflexus aurantiacus*. *Biochim. Biophys. Acta* **1999**, *1413*, 172−180.

(10) Prokhorenko, V. I.; Holzwarth, A. R.; Müller, M. G.; Schaffner, K.; Miyatake, T.; Tamiaki, H. Energy Transfer in Supramolecular Artificial Antennae Units of Synthetic Zinc Chlorins and Co-aggregated Energy Traps. A Time-Resolved Fluorescence Study. *J. Phys. Chem. B* **2002**, *106*, 5761−5768.

(11) Tang, K.-H.; Zhu, L.; Urban, V. S.; Collins, A. M.; Biswas, P.; Blankenship, R. E. Temperature and Ionic Strength Effects on the Chlorosome Light-Harvesting Antenna Complex. *Langmuir* **2011**, *27*, 4816−4828.

(12) Borisov, A. Y. On the Structure and Function of "Chlorosomes" of Green Bacteria. *Biophysics* **2012**, *57*, 562−564.

(13) Olson, J. M. The FMO Protein. *Photosynth. Res.* **2004**, *80*, 181−187.

(14) Milder, M. T. W.; Brüggemann, B.; van Grondelle, R.; Herek, J. L. Revisiting the Optical Properties of the FMO Protein. *Photosynth. Res.* **2010**, *104*, 257−274.

(15) Blankenship, R. E. *Molecular Mechanism of Photosynthesis*; Blackwell Science: Oxford, U.K., 2002.

(16) Frigaard, N.-U.; Li, H.; Martinsson, P.; Das, S. K.; Frank, H. A.; Aartsma, T. J.; Bryant, D. A. Isolation and Characterization of Carotenosomes from a Bacteriochlorophyll *c*-less Mutant of *Chlorobium tepidum*. *Photosynth. Res.* **2005**, *86*, 101−111.

(17) Pedersen, M. Ø.; Underhaug, J.; Dittmer, J.; Miller, M.; Nielsen, N. C. The Three-Dimensional Structure of CsmA: A Small Antenna Protein from the Green Sulfur Bacterium *Chlorobium tepidum*. *FEBS Lett.* **2008**, *582*, 2869−2874.

(18) Feick, R. G.; Fuller, R. C. Topography of the Photosynthetic Apparatus of *Chloroflexus aurantiacus*. *Biochemistry* **1984**, *23*, 3693−3700.

(19) Montaño, G. A.; Wu, H.-M.; Lin, S.; Brune, D. C.; Blankenship, R. E. Isolation and Characterization of the B798 Light-Harvesting Baseplate from the Chlorosomes of *Chloroflexus aurantiacus*. *Biochemistry* **2003**, *42*, 10246−10251.

(20) Linnanto, J. M.; Korppi-Tommola, J. E. I. Exciton Description of Chlorosome to Baseplate Excitation Energy Transfer in Filamentous Anoxygenic Phototrophs and Green Sulfur Bacteria. *J. Phys. Chem. B* **2013**, *117*, 11144−11161.

(21) Bryant, D. A.; Vassilieva, E. V.; Frigaard, N.-U.; Li, H. Selective Protein Extraction from *Chlorobium tepidum* Chlorosomes Using Detergents. Evidence That CsmA Forms Multimers and Binds Bacteriochlorophyll *a*. *Biochemistry* **2002**, *41*, 14403−14411.

(22) Pedersen, M. Ø.; Linnanto, J.; Frigaard, N.-U.; Nielsen, N. C.; Miller, M. A Model of the Protein−Pigment Baseplate Complex in Chlorosomes of Photosynthetic Green Bacteria. *Photosynth. Res.* **2010**, *104*, 233−243.

(23) Kovács, S. Á.; Bricker, W. P.; Niedzwiedzki, D. M.; Colletti, P. F.; Lo, C. S. Computational Determination of the Pigment Binding Motif in the Chlorosome Protein A of Green Sulfur Bacteria. *Photosynth. Res.* **2013**, *118*, 231−247.

(24) Huh, J.; Saikin, S. K.; Brookes, J. C.; Valleau, S.; Fujita, R.; Aspuru-Guzik, A. Atomistic Study of Energy Funneling in the Light-Harvesting Complex of Green Sulfur Bacteria. *J. Am. Chem. Soc.* **2014**, *136*, 2048−2057.

(25) Fujita, T.; Brookes, J. C.; Saikin, S. K.; Aspuru-Guzik, A. Memory-Assisted Exciton Diffusion in the Chlorosome Light-Harvesting Antenna of Green Sulfur Bacteria. *J. Phys. Chem. Lett.* **2012**, *3*, 2357−2361.

(26) Savikhin, S.; Zhu, Y.; Lin, S.; Blankenship, R. E.; Struve, W. S. Femtosecond Spectroscopy of Chlorosome Antennas from the Green Photosynthetic Bacterium *Chloroflexus aurantiacus*. *J. Phys. Chem.* **1994**, *98*, 10322−10334.

(27) Savikhin, S.; van Noort, P. I.; Zhu, Y.; Lin, S.; Blankenship, R. E.; Struve, W. S. Ultrafast Energy Transfer in Light-Harvesting Chlorosomes from the Green Sulfur Bacterium *Chlorobium tepidum*. *Chem. Phys.* **1995**, *194*, 245−258.

(28) Martiskainen, J.; Linnanto, J.; Aumanen, V.; Myllyperkiö, P.; Korppi-Tommola, J. Excitation Energy Transfer in Isolated Chlorosomes from *Chlorobaculum tepidum* and *Prosthecochloris aestuarii*. *Photochem. Photobiol.* **2012**, *88*, 675−683.

(29) Fetisova, Z.; Freiberg, A.; Mauring, K.; Novoderezhkin, V.; Taisova, A.; Timpmann, K. Excitation Energy Transfer in

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702−2707

Chlorosomes of Green Bacteria: Theoretical and Experimental Studies. *Biophys. J.* **1996**, *71*, 995−1010.
(30) Pšenčík, J.; Polívka, T.; Němec, P.; Dian, J.; Kudrna, J.; Malý, P.; Hála, J. Fast Energy Transfer and Exciton Dynamics in Chlorosomes of the Green Sulfur Bacterium *Chlorobium tepidum*. *J. Phys. Chem. A* **1998**, *102*, 4392−4398.
(31) Prokhorenko, V. I.; Steensgaard, D. B.; Holzwarth, A. R. Exciton Dynamics in the Chlorosomal Antennae of the Green Bacteria *Chloroflexus aurantiacus* and *Chlorobium tepidum*. *Biophys. J.* **2000**, *79*, 2105−2120.
(32) Dostál, J.; Vácha, F.; Pšenčík, J.; Zigmantas, D. 2D Electronic Spectroscopy Reveals Excitonic Structure in the Baseplate of a Chlorosome. *J. Phys. Chem. Lett.* **2014**, *5*, 1743−1747.
(33) Kell, A.; Acharya, K.; Blankenship, R. E.; Jankowiak, R. On Destabilization of the Fenna−Matthews−Olson Complex of *Chlorobaculum tepidum*. *Photosynth. Res.* **2014**, *120*, 323−329.
(34) Jankowiak, R.; Reppert, M.; Zazubovich, V.; Pieper, J.; Reinot, T. Site Selective and Single Complex Laser-Based Spectroscopies: A Window on Excited State Electronic Structure, Excitation Energy Transfer, and Electron−Phonon Coupling of Selected Photosynthetic Complexes. *Chem. Rev.* **2011**, *111*, 4546−4598.
(35) Psencik, J.; Schaafsma, T. J.; Searle, G. F. W.; Hala, J. Fluorescence Detected Magnetic Resonance of Monomers and Aggregates of Bacteriochlorophylls of Green Sulfur Bacteria *Chlorobium* sp. *Photosynth. Res.* **1997**, *52*, 83−92.
(36) *Persistent Spectral Hole-Burning: Science and Applications*; Moerner, W. E., Ed.; Topics in Current Physics; Springer: Berlin, Germany, 1988; Vol. *44*.
(37) Miller, M.; Cox, R. P.; Olson, J. M. Low-Temperature Spectroscopy of Isolated FMO-Protein and a Membrane-Free Reaction Center Complex from the Green Sulfur Bacterium *Chlorobium tepidum*. *Photosynth. Res.* **1994**, *41*, 97−103.
(38) He, G.; Niedzwiedzki, D. M.; Orf, G. S.; Zhang, H.; Blankenship, R. E. Dynamics of Energy and Electron Transfer in the FMO-Reaction Center Core Complex from the Phototrophic Green Sulfur Bacterium *Chlorobaculum tepidum*. *J. Phys. Chem. B* **2015**, DOI: 10.1021/acs.jpcb.5b04170.
(39) Richert, R.; Bässler, H. Energetic Relaxation of Triplet Excitation in Vitreous Benzophenone. *Chem. Phys. Lett.* **1985**, *118*, 235−239.
(40) Movaghar, B.; Grünewald, M.; Ries, B.; Bässler, H.; Würtz, D. Diffusion and Relaxation of Energy in Disordered Organic and Inorganic Materials. *Phys. Rev. B* **1986**, *33*, 5545−5554.
(41) Feng, X.; Neupane, B.; Acharya, K.; Zazubovich, V.; Picorel, R.; Seibert, M.; Jankowiak, R. Spectroscopic Study of the CP43 Complex and the PSI-CP43′ Supercomplex of the Cyanobacterium *Synechocystis* PCC 6803. *J. Phys. Chem. B* **2011**, *115*, 13339−13349.

DOI: 10.1021/acs.jpclett.5b01074
J. Phys. Chem. Lett. 2015, 6, 2702−2707