Supporting Material.

Conformational Switching in a Light-Harvesting Protein as Followed by Single-Molecule Spectroscopy

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The authors declare no conflict of interest

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Absorption spectroscopy.

Fig. SI1 displays the UV-vis-NIR electronic absorption spectra of LH2 complexes purified from *Rdv. sulfidophilum* equilibrated in buffers at pH 8.5, 7.5 and 7.0. As previously published (1) lowering the pH from 8.5 to 7.0 induces a ~20 nm blue shift of the lower energy transition of these complexes from 853 to 833 nm, while the carotenoid-absorbing region is unperturbed indicating that the overall quaternary structure is conserved [2].

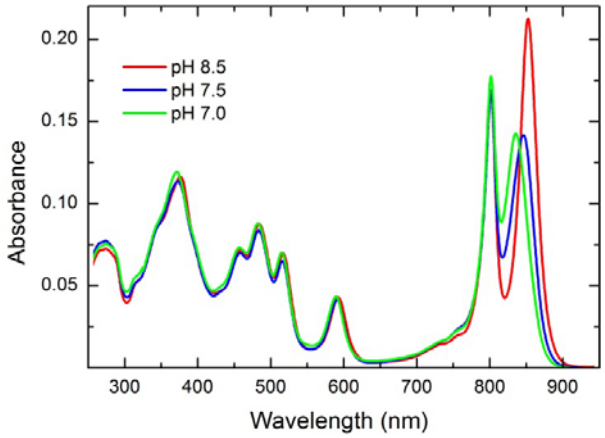

Fig. SI1. Room-temperature UV-vis-NIR electronic absorption spectra of LH2 complexes purified from *Rdv. sulfidophilum* equilibrated in buffers at pH 8.5, 7.5 and 7.0.

Redfield exciton model.

The NIR electronic spectrum of LH2 from *Rdv. sulfidophilum* at pH=8.5 can be reproduced using the same exciton model that has been employed to quantitatively fit other LH2 complexes (3-5). Most of the previous studies were characterized by a spectral disorder of the order of 500 cm^{-1}. Initially a value of 500 cm^{-1} was used for the disorder; however, this was reduced to 250 cm^{-1} in an alternate model. In this case, the reduced disorder was concomitant with an increase in phonon coupling. Both models gave similar fits of the bulk absorption spectra, but the statistics of spectral fluctuations observed in the SMS experiment can be reproduced only by the alternative model with its small disorder.

In Fig. SI2 the statistics of the fluorescence band width (fwhm) are plotted as a function of the peak position for the two exciton models as well as the experimental data at pH=8.5 (red) and pH=7.5 (blue). In the first example we compare the measured statistics with the normal model with a large disorder of 500 cm^{-1} (3). Such a model describes well the SMS

dynamics observed for LH2 complexes from different bacteria (see Ref. 3). Besides jumps with small amplitudes (within 10 nm) there are big jumps to the blue and to the red (the latter case is characterized by big broadening and changes in asymmetry of the fluorescence band). Small and big jumps correspond to a two conformational coordinates producing the shifts of the site energies that are smaller than, or comparable to, the pigment-pigment coupling (250-300 cm^{-1} for the B850 band), or significantly exceed it (thus producing dramatic changes in the exciton structure of the complex) (6). However, in the case of *Rdv. sulfidophilum*, with its additional pH-dependent blue-shift, such a model doesn't work as the distribution of fluorescence band width is too large.

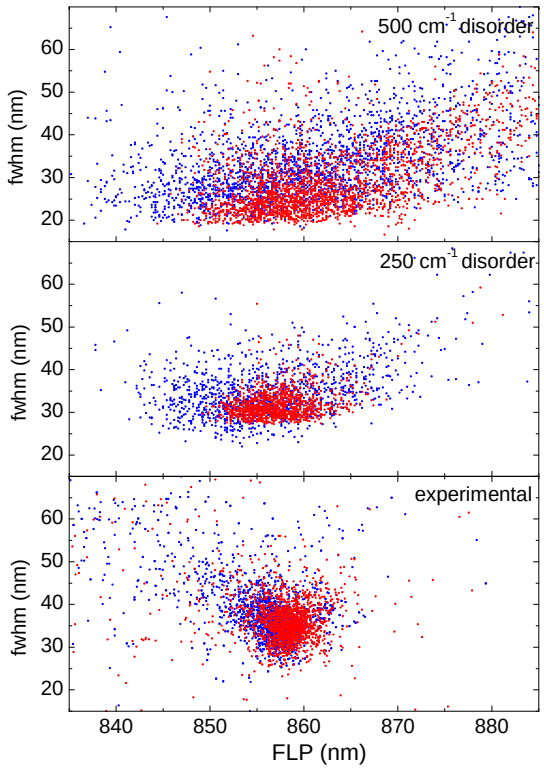

Fig. SI2. Comparison of the width (fwhm) of the fluorescence peak (FLP) position obtained from the two exciton models having disorder values of 500 cm^{-1} (top) and 250 cm^{-1} (middle) with the experimental data (bottom) at pH = 8.5 (red) and pH = 7.5 (blue).

Looking at the experimental data we may conclude that only small jumps (mostly within 10 nm) are present *in Rdv. sulfidophilum* LH2 when poised at pH=8.5. So, probably only one conformational coordinate is active, responsible for relatively small spectral shifts of individual pigments (i.e. no more than 300 cm^{-1}). This situation can be modelled by imposing

the disorder value of 250 cm^{-1} in our alternative model. We can further suppose that lowering in pH activates another conformational coordinate that can produce big spectral shifts, more specifically, the 500 cm^{-1} blue-shifts. Such a model is not only consistent with the pH-dependent bulk spectra (see Fig. 1), but also gives better agreement with the measured statistics.

The minimal model capable to explain the observed SMS dynamics for *Rbl. acidophilus* LH2 includes one coordinate with two conformational states, shifting the site energies by 190 cm^{-1} to the blue or to the red, and second coordinate with two more conformational states, creating larger shifts, *i.e.* 440 cm^{-1} to the blue or to the red (the so-called four-state model (6**)**). The minimal model for *Rdv. sulfidophilum* LH2 should be thus a three-state one, including the two states responsible for small spectral fluctuations and the third state (pH-dependent) with the big (about 500 cm^{-1}) blue shift. In this work a more general description of small shifts (Gaussian distribution instead of just two discrete states) was employed, but still restricted to a just one discrete conformational state responsible for large blue shifts.

References

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