Supporting Information

Excitation Energy Trapping and Dissipation by Ni-Substituted Bacteriochlorophyll a in Reconstituted LH1 Complexes from *Rsp. rubrum*

Lambrev, P. H.; Miloslavina, Y.; van Stokkum, I. H. M.; Stahl, A. D.; Michalik, M.; Susz, A.; Tworzydło, J.; Fiedor, J.; Huhn, G.; Groot, M.-L.; van Grondelle, R.; Garab, G.; Fiedor, L.

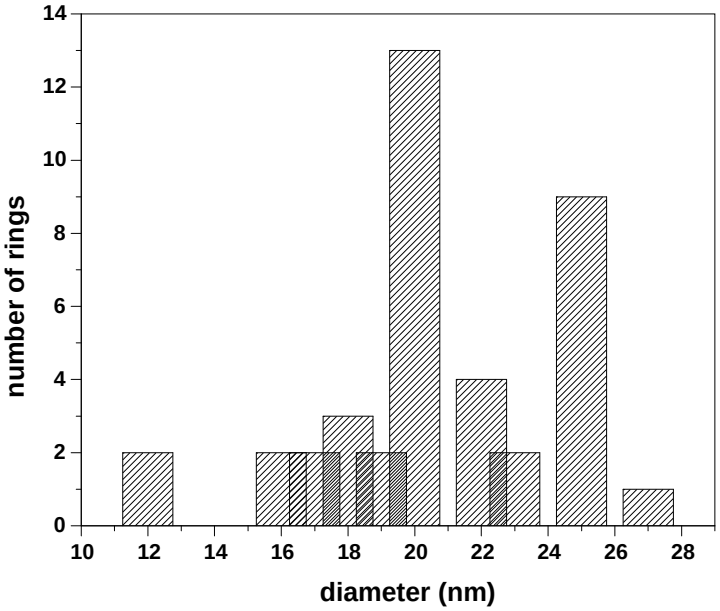

Figure S1. Distribution of ring diameters in Crt-less Ni-LH1 scanned with a surface probe microscrope (AFM) using a MiroMasch Hi'RES-W14 cantilever. The comparatively wide and apparently bimodal distribution reveals that the LH1 structure, at least in the absence of detergent, is flexible and leads to variability in ring size and shape.

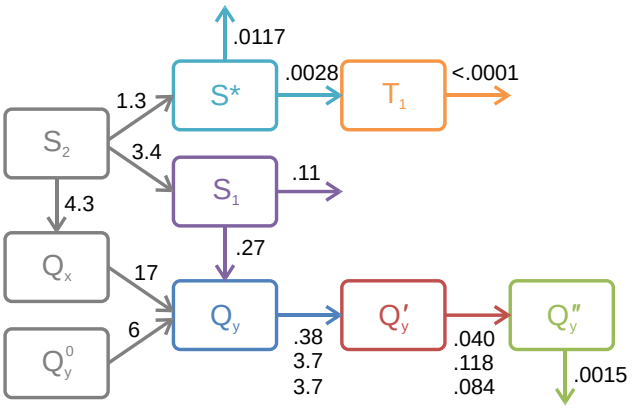

Figure S2. Kinetic scheme of the model used for simultaneous global target analysis of the TA data obtained from control Sph-LH1. The compartments S_2, S_1, S*, and T_1 represent Sph excited states and Q_x, Q_y^0, and Q_y represent BChl excited states. The initially populated compartments were S_2¸Q_x, and Q_y^0 for 509, 590, and 860 nm pump wavelength, respectively. The data were fitted with the same set of rate constants (indicated in ps^{-1}), except for the $Q_y \rightarrow Q_y'$ and $Q_y' \rightarrow Q_y''$ relaxation, which was fitted with independent rate constants for 509, 590, and 860 nm (values top to bottom).

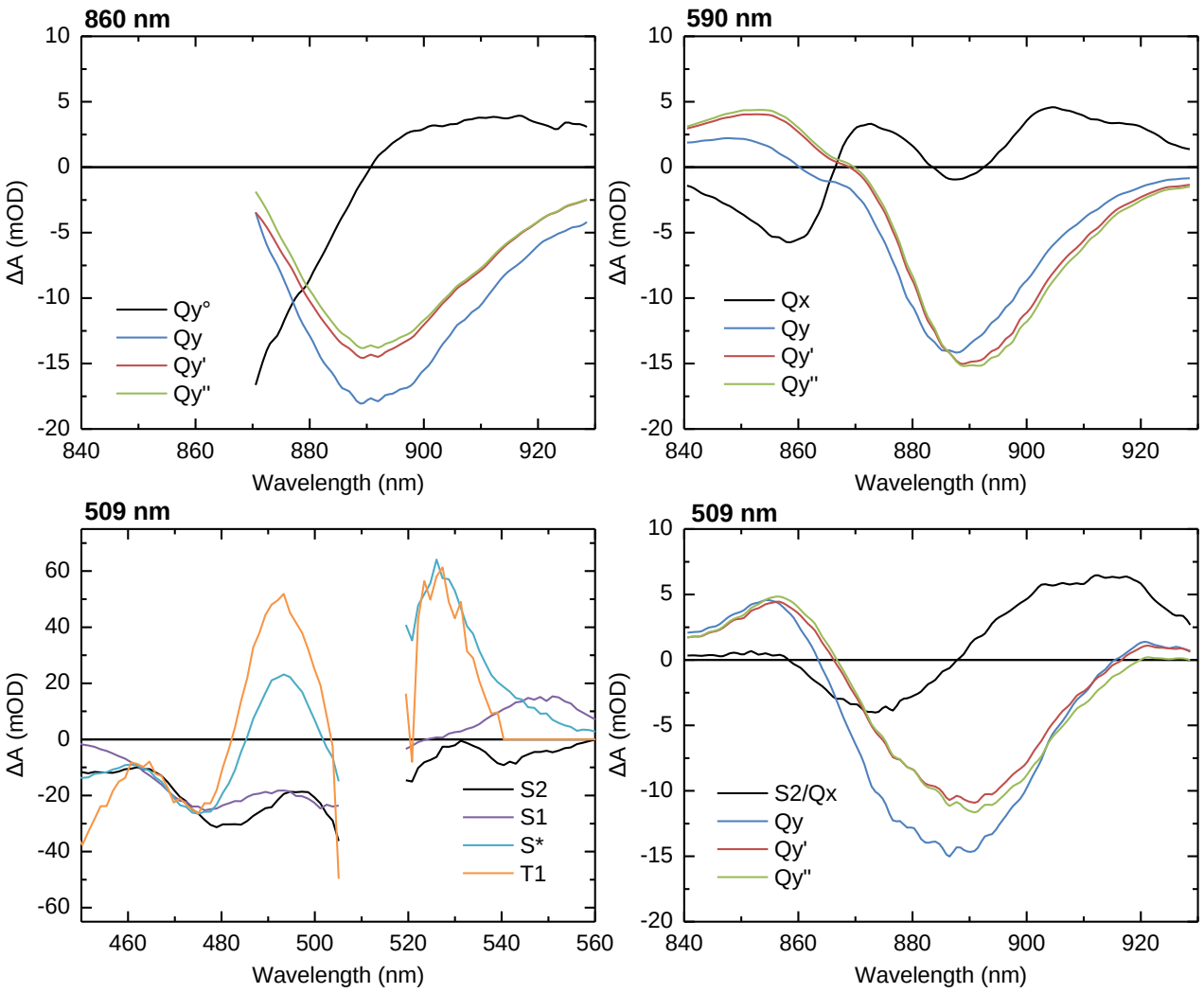

Figure S3. Species-associated absorption difference spectra (SADS) resulting from global target analysis of the TA data for control Sph-LH1, performed using the kinetic model shown in Fig. S2.

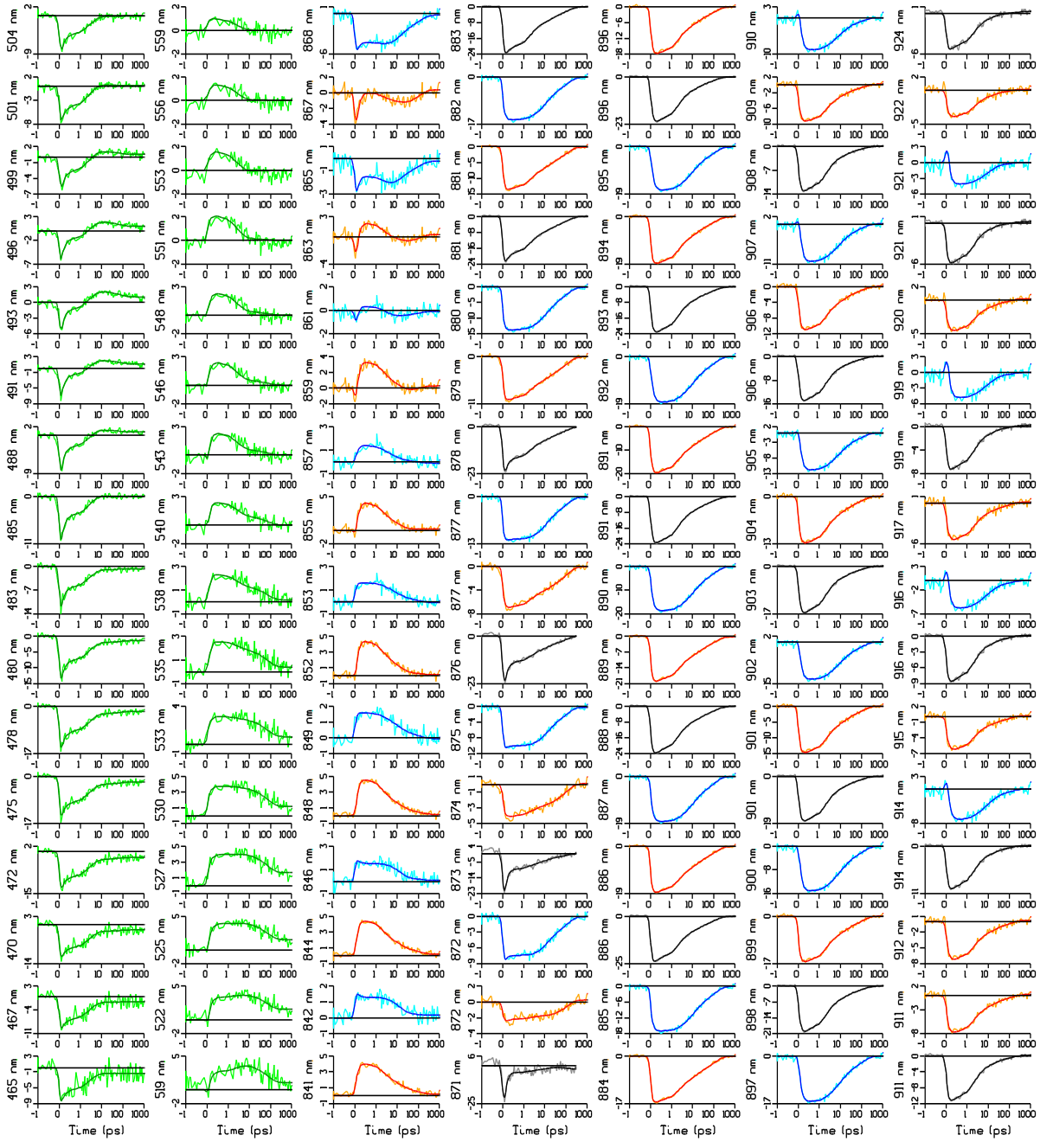

Fig. S4. Selected measured (light color) and fitted (dark color) time traces of TA data of Sph-Ni-LH1. The probe wavelength is written as ordinate label. Time axis is linear from –1 to 1 ps, relative to the location of the IRF maximum, and logarithmic thereafter. Pump wavelengths: 509 nm (green and blue), 590 nm (red), 860 nm (black).

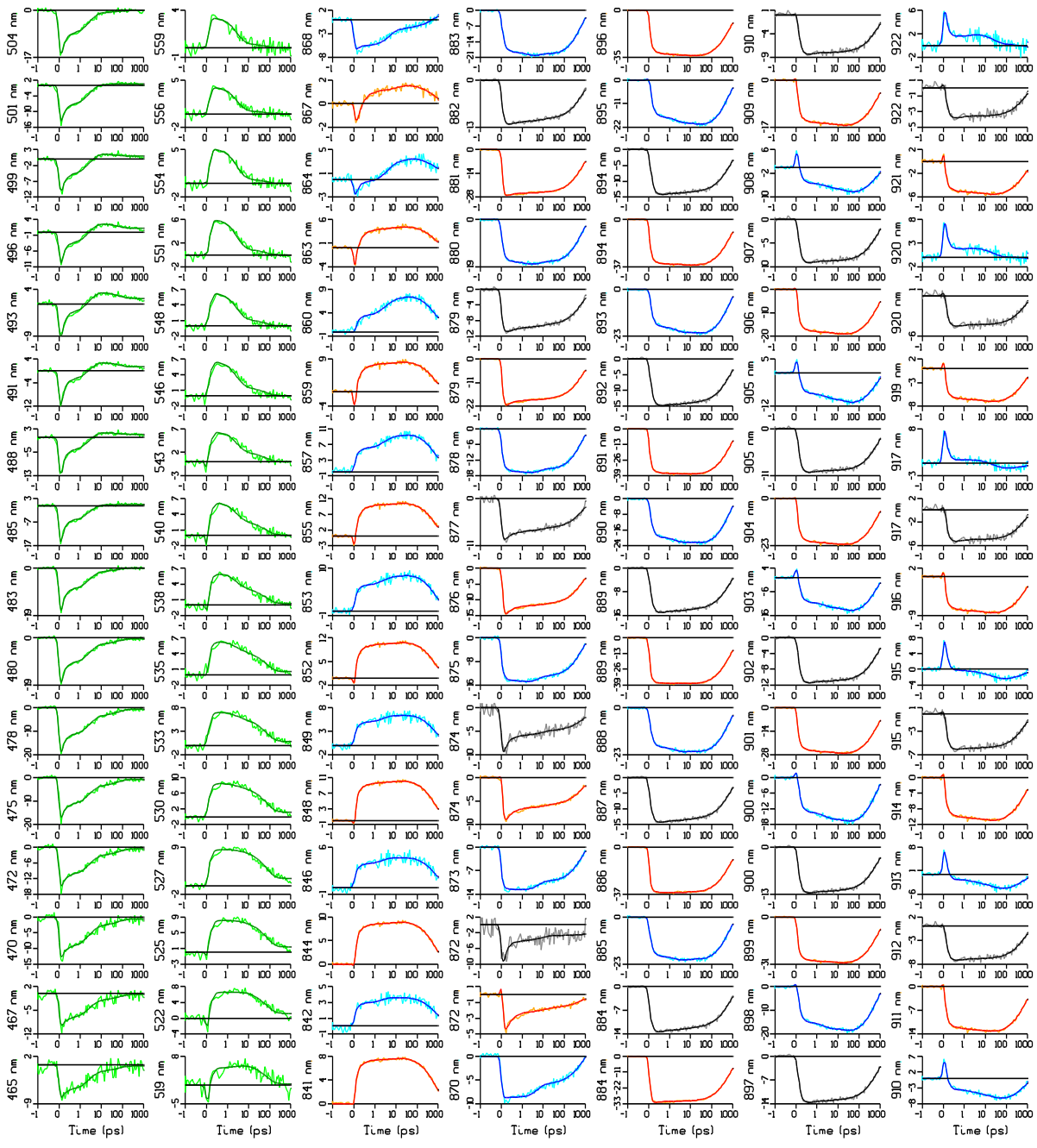

Fig. S5. Selected measured (light color) and fitted (dark color) time traces of TA data of Sph-LH1. The probe wavelength is written as ordinate label. Time axis is linear from –1 to 1 ps, relative to the location of the IRF maximum, and logarithmic thereafter. Pump wavelengths: 509 nm (green and blue), 590 nm (red), 860 nm (black).

Residual Analysis

The matrix of residuals of each experiment was systematically analyzed with the help of the Singular Value Decomposition (SVD). Formally the residual matrix can be decomposed as

$$res(t,\lambda) = \sum_{l=1}^{m} u_l^{res}(t) s_l w_l^{res}(\lambda)$$

where u_l and w_l are the left and right singular vectors, s_l the sorted singular values, and m is the minimum of the number of rows and columns of the matrix. The singular vectors are orthogonal, and provide an optimal least squares approximation of the matrix. The SVD is useful to diagnose shortcomings of the model used, or systematic errors in the data. In particular, the $u_1^{res}(t)$ in the left hand part of Figures S6 and S7 show no trends. The $w_1^{res}(t)$ in the right hand part show that the Signal to Noise ratio is wavelength dependent, mainly due to absorption spectrum. Taking together the quality of the fit (Figures S4 and S5) and the absence of trends in the left singular vectors (left hand parts of Figures S6 and S7) the fits are considered satisfactory.

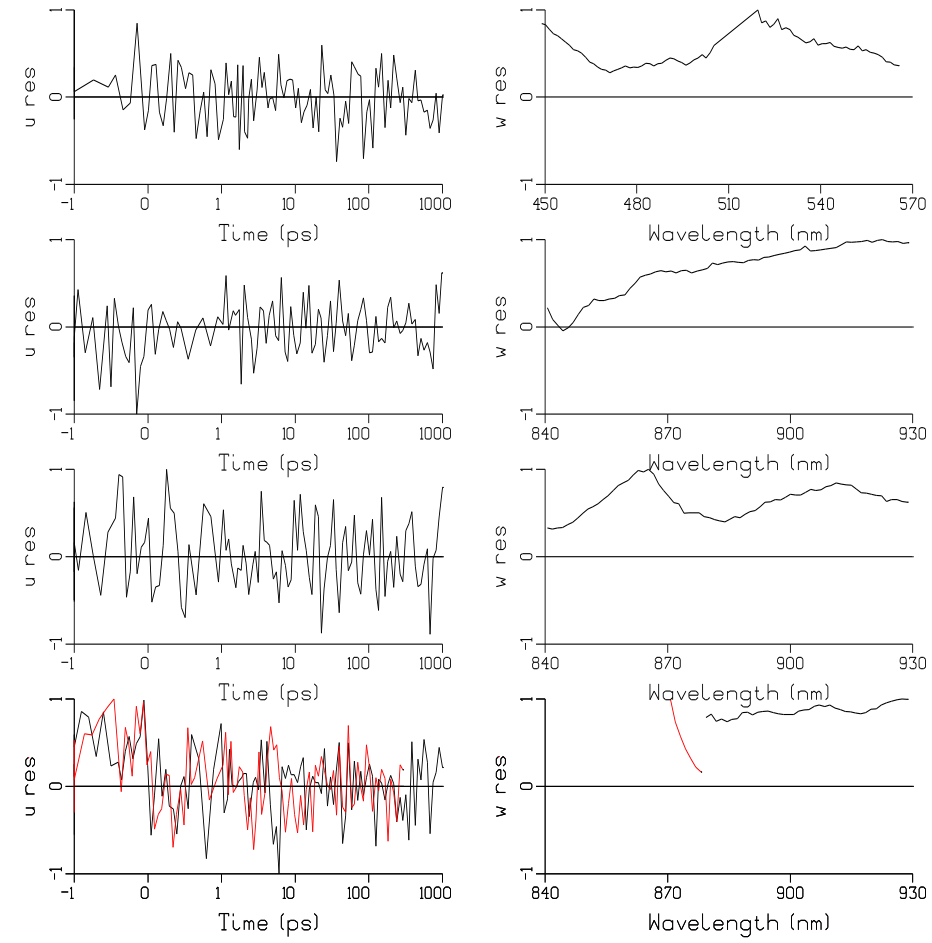

Figure S6. Singular value decomposition (SVD) of the matrix of residuals of transient difference absorption data of Sph-Ni-LH1. From top to bottom: 509 nm exc VIS and NIR, 600 nm exc NIR, 860 nm exc NIR. From left to right: first left singular vector, $u_{\mathrm{res},1}$, (note that the time axis is linear from -1 till 1 ps relative to the location of the IRF maximum, and logarithmic thereafter) first right singular vector, $w_{\mathrm{res},1}$.

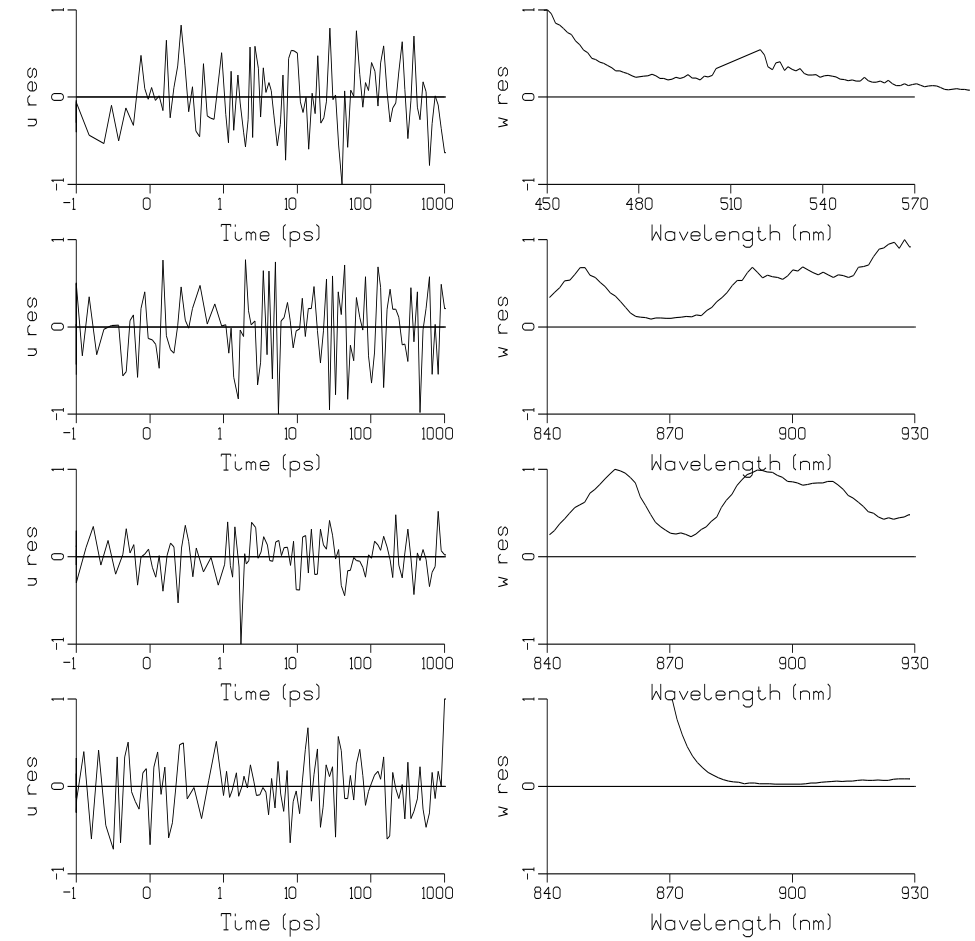

Figure S7. Singular value decomposition (SVD) of the matrix of residuals of transient difference absorption data of Sph-LH1. From top to bottom: 509 nm exc VIS and NIR, 600 nm exc NIR, 860 nm exc NIR. From left to right: first left singular vector, $u_{\mathrm{res},1}$, (note that the time axis is linear from -1 till 1 ps relative to the location of the IRF maximum, and logarithmic thereafter) first right singular vector, $w_{\mathrm{res},1}$.