

Supplementary Information

Mixing of exciton and charge-transfer states in light-harvesting complex Lhca4

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1. Basic equations

In the modified Redfield picture the absorption (OD), linear dichroism (LD), steady-state non-selective fluorescence (FL), and magic angle Stark absorption (SA) spectra are given by (Mukamel, 1995; Zhang et al., 1998; Novoderezhkin et al., 2004a; 2007):

$$\begin{aligned}
 OD(\omega) &= \omega \sum_k \mathbf{d}_{kg}^2 \text{Im}\{L_{kg}\}; \\
 LD(\omega) &= \omega \sum_k \left(-d_{kgz}^2 + \frac{1}{2}d_{kgx}^2 + \frac{1}{2}d_{kgy}^2\right) \text{Im}\{L_{kg}\}; \\
 FL(\omega) &= \omega^3 \sum_k P_k \mathbf{d}_{kg}^2 \text{Im}\{L_{kg}^F\}; \\
 SA(\omega) &= \omega \text{Im} \left\{ \sum_{kk''} L_{k'g} L_{kg} [(\mathbf{d}_{kg} \mathbf{d}_{gk''})(\mathbf{d}_{k''k'} \mathbf{d}_{k'k}) L_{k''g} + \frac{2}{\omega} (\mathbf{d}_{k'k} \mathbf{d}_{gk''})(\mathbf{d}_{kg} \mathbf{d}_{k''k'})] + \right. \\
 &\quad \left. + \sum_{kk'} L_{k'g} L_{kg} \frac{1}{\omega} (\mathbf{d}_{kg} \mathbf{d}_{gk'}) \sum_n c_n^k c_n^{k'} (\mathbf{d}_{nn}^2 - 2\mathbf{d}_n^2) \right\} \\
 L_{kg} &= i \int_0^\infty dt \exp \left\{ i(\omega - \omega_{kg})t - \sum_n (c_n^k)^4 g(t) - \frac{t}{2\tau_k} \right\}; \\
 L_{kg}^F &= i \int_0^\infty dt \exp \left\{ i(\omega - \omega_{kg})t + 2it \sum_n (c_n^k)^4 \lambda - \sum_n (c_n^k)^4 g^*(t) - \frac{t}{2\tau_k} \right\}; \\
 \mathbf{d}_{kg} &= \sum_n c_n^k \mathbf{d}_n \quad ; \quad \mathbf{d}_{k'k} = \sum_n c_n^{k'} c_n^k \Delta \mathbf{d}_n \quad ; \quad \frac{1}{\tau_k} = - \sum_{k' \neq k} R_{k'k'kk}
 \end{aligned} \tag{S1}$$

where P_k denote the steady-state population of the k -th state, ω_{kg} is the energy of pure electronic transition from the ground to k -th exciton state (emerging from diagonalization of the free-exciton Hamiltonian, i.e. these energies do not contain reorganization shift and therefore they are different from the energies of the zero-phonon transitions), \mathbf{d}_{kg} is the dipole moment corresponding to transition from the ground to the k -th exciton state, $\mathbf{d}_{k'k}$ is the dipole moment corresponding to transitions between the exciton states k and k' (these dipoles are expressed through through the $S_0 \rightarrow S_1$ transition dipoles \mathbf{d}_n and the difference between the S_1 and S_0 permanent dipoles $\Delta \mathbf{d}_n$ for the n -th diabatic state). The SA spectrum also contains the $S_1 \rightarrow S_2$ (\mathbf{d}_{nn}) transition dipoles for the n -th diabatic state. The d_{kgz} denote projection of the dipole moment to the z -axis normal to the membrane plane, d_{kgx} d_{kgy} are projections to the x - and y -axes in the membrane plane. The wavefunction amplitudes c_n^k give the participation of the n -th pigment (diabatic state) in the k -th exciton state. Coupling to phonons is accounted for through the line-broadening function $g(t)$ and reorganization energy λ . The relaxation-induced broadening is given by the inverse lifetime of the exciton state τ_k (the latter is expressed as the sum of transfer rates $R_{k'k'kk}$ from k -th to other ($k' \neq k$) states). The transfer rates are given by the modified Redfield tensor as described elsewhere (Zhang et al., 1998). Notice that Eqs. S1 give homogeneous line shapes, i.e. including the relaxation-induced and phonon-induced broadening. In the presence of static disorder (for example site inhomogeneity) the homogeneous

spectra should be averaged over a random distribution of the site energies that will perturb the energies ω_{kg} and eigenfunctions c_n^k of the exciton states.

The line-broadening function $g(t)$ and reorganization energy in the site representation λ are:

$$g(t) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega^2} C(\omega) \left[\coth \frac{\omega}{2k_B T} (\cos \omega t - 1) - i(\sin \omega t - \omega t) \right] \quad (S2)$$

$$\lambda = - \lim_{t \rightarrow \infty} \frac{d}{dt} \text{Im} \{g(t)\} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega} C(\omega)$$

where $C(\omega)$ is the spectral density of exciton-phonon coupling, k_B is the Boltzmann constant, T is the temperature. Notice that the lineshape function $g(t)$ and the reorganization energy λ in the exciton representation are smaller than in the site representation being multiplied by the participation ratio $\sum_n (c_n^k)^4$ (which is equal to the inverse delocalization length of individual exciton states). For instance, the energy of the zero-phonon transition of the k -th exciton state is:

$$\omega_{kg}^0 = \omega_{kg} - \sum_n (c_n^k)^4 \lambda \quad (S3)$$

To construct the spectral density profile we use the Brownian oscillator model that includes the low-frequency overdamped part and underdamped terms reflecting a coupling to the high-frequency vibrations:

$$C(\omega) = 2\lambda_0 \frac{\omega\gamma_0}{\omega^2 + \gamma_0^2} + \sum_j 2\lambda_j \omega_j^2 \frac{\omega\gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2\gamma_j^2} \quad ; \quad \lambda_j = S_j \omega_j \quad (S4)$$

$$\lambda = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega} C(\omega) = \lambda_0 + \sum_j \lambda_j$$

where λ_0 and γ_0 denote coupling and characteristic frequency of m -th Brownian oscillator, ω_j , S_j , λ_j and γ_j are frequency, Huang-Rhys factor, coupling and damping constant for the j -th vibrational mode.

In the presence of disorder, the contributions of the pigments (diabatic states) to the exciton states can be characterized by calculating the density of exciton states D_k together with distribution of the pigment participations D_n (Raszewski et al., 2005):

$$D_k(\omega) = \left\langle \delta(\omega - \omega_{kg}^0) \right\rangle \quad (S5)$$

$$D_n(\omega) = \left\langle \sum_k (c_n^k)^2 \delta(\omega - \omega_{kg}^0) \right\rangle$$

The function $D_n(\omega)$ shows participation of the n -th pigment to all the exciton states with the energy $\omega_{kg}^0 = \omega$.

2. Transition dipoles and exciton couplings

We assume that the dipoles of the Chls Q_y transitions are directed from the N_B to the N_D atoms and the distances between the dipoles are equal to the distances between the Mg atoms of the two Chls. The transition dipoles, the center coordinates (corresponding to Mg atoms), and the center-to-center distances for the pigments 601-618 of the Lhca4 complex are given in Tables S1 and S2. Following our modeling of LHCII (Novoderezhkin et al., 2005) the effective dipole strength of Chls is estimated as $f^2 d^2 / \epsilon$ (where d is the vacuum transition dipole, f is the local field correction factor, and ϵ is the relative dielectric constant). For the light-harvesting Chls we suppose $\epsilon = n^2$, where $n = 1.54$ is the refractive index of the protein. Knox and Spring have shown (Knox and Spring, 2003) that $f^2 d^2 = 33.1$ and 24 Debye² (D^2) for Chl a and Chl b , respectively (at $n = 1.54$). Then, the effective dipole strength for Chl a equals to $f^2 d^2 / n^2 = 13.9$ D^2 . This value corresponds to the Q_y '0-0' transition, so that the full strength of the Q_y transition is probably 20% larger (as pointed out by Knox and Spring). In our study of LHCII (Novoderezhkin et al., 2005) the effective dipole strength for Chl a is varied in the 14-18 D^2 range (with the corresponding scaling of the Chl b dipole strength). The best fit of the linear spectra and nonlinear kinetics was obtained for a value of 16 D^2 for Chl a (and 11.6 D^2 for Chl b). In our modeling of LHCII these values have been used to calculate the pigment-pigment couplings in the point-dipole approximation (Novoderezhkin et al., 2005). Later the exciton couplings for LHCII have been calculated also with more sophisticated methods (Frähmcke and Walla, 2006; Müh et al., 2010; 2012; Chmeliov et al 2015). Müh et al. (2010) compared the results obtained for LHCII with different methods and noticed a very good correlation between the couplings calculated with their PTrEsp method and with the point dipole approximation used in our study (Novoderezhkin et al., 2005). Therefore, we conclude that the point dipole approximation can be used as a first step in modeling of the Lhca4 complex whose structure is very similar to LHCII. The couplings calculated for Lhca4 in the point-dipole approximation are shown in Table S3.

3. Static dipoles and S_2 - S_1 transition dipoles

The S_2 - S_1 transition dipole d_{nn} for Chls is responsible for additional contributions to the excited-state absorption (ESA) (in the third-order nonlinear responses like pump-probe, 2D-echo, etc., including also the steady-state Stark response). In principle the S_2 - S_1 manifold includes a lot of transitions (in pump-probe they give a broad ESA wing). The simplest way to account for this feature is the three-level model (Kühn et al., 1996), where each Chl contains a single S_1 and single S_2 level (giving just one S_2 - S_1 transition). The ratio of the S_2 - S_1 and S_1 - S_0 transition dipoles is not known and typically is varied from 0 to 2 (Kühn et al., 1996). A reasonable fit of the nonlinear spectra (for example, pump-probe) has been obtained with the S_2 - S_1 dipoles around 1 (in the units of the S_1 - S_0 dipole). (Meier et al., 1997). The exact value is determined from the fit of the spectra. In our previous models of LHCII this value was varied from 0.4 to 1.2 giving the best fit of pump-probe spectra at 0.65 (Novoderezhkin et al., 2005). In the present modeling of Lhca4 we have varied the S_2 - S_1 transition dipole around the same value of 0.65 and we have found that the best fit of the Stark spectra can be obtained with the value of 0.7. Remarkably, the two values determined from the fit of the two different nonlinear responses are close to each other.

The static (permanent) dipole Δd_n was estimated as 1.4-1.8 D for Chls a in PSII-RC (Frese et al., 2003). Stark spectroscopy studies of LHCII complex gave values of 0.6 and 2.0 D for Chls a and Chls b , respectively (Palacios et al., 2003). Based on these results we use the value of 1.0 D for Chl a . In order to reproduce the relative amplitudes of the SA peaks the static dipole for Chl b should be increased to 2.8 D. Thus, the ratio of the static dipoles for Chls a and b (adjusted from our fit) is close to that determined experimentally for LHCII (Palacios et al., 2003). In our modeling the static dipole moments of Chls a and b are supposed to be parallel to the corresponding transition dipoles. The static dipole for CT has been estimated as 30 D in our modeling of the SA spectra of the PSII-RC (Novoderezhkin et al., 2007). Adjustment of this value from the fit of the SA amplitudes for Lhca4 gave the value of 20 D.

Table S1. Transition dipole components dx, dy, dz (Debye) and center coordinates Rx, Ry, Rz (nm) for the pigments 601-618 of the Lhca4 complex. The z-axis corresponds to the normal to the membrane plane. The absolute values of the dipoles are 4 and 3.4 D for Chls *a* and *b*, respectively.

Pigment	dx	dy	dz	Rx	Ry	Rz
<i>a</i> 601	3.1309	-2.4552	-0.4113	2.0032	1.7274	23.5366
<i>a</i> 602	3.6497	-1.5714	-0.4587	3.2518	1.5771	23.8544
<i>a</i> 603	-3.6678	-0.2202	-1.5807	4.1795	1.0559	23.3284
<i>a</i> 604	0.0237	-2.2356	3.3169	4.8400	2.1828	21.9371
<i>b</i> 606	-2.3285	-0.8765	2.3259	5.4467	1.6908	22.3123
<i>b</i> 607	-2.4219	0.4931	2.3433	4.9184	0.9735	22.0316
<i>b</i> 608	3.2035	0.4708	-1.0564	5.2382	2.2855	23.7886
<i>a</i> 609	3.7923	-1.2006	0.4203	4.9901	1.2821	23.6276
<i>a</i> 610	-3.6579	0.5006	-1.5392	4.2227	2.8237	23.5473
<i>a</i> 611	-3.9042	0.8699	0.0148	2.4641	2.7486	23.1815
<i>a</i> 612	3.5246	-0.5193	-1.8186	3.3461	2.8695	22.7491
<i>a</i> 613	-0.1313	3.5834	1.7725	2.8323	1.3393	21.9802
<i>a</i> 614	-1.5317	2.2223	-2.9522	2.1383	1.8741	21.6396
<i>a</i> 617	-0.9825	-1.4111	-3.6116	5.7944	0.7188	23.9158
<i>b</i> 618	1.9903	-2.3964	-1.3770	6.1482	2.9553	23.9606

Table S2. Distances between the transition dipoles, calculated as distances between the Mg atoms of the pigments 601-618.

	<i>a</i> 601	<i>a</i> 602	<i>a</i> 603	<i>a</i> 604	<i>b</i> 606	<i>b</i> 607	<i>b</i> 608	<i>a</i> 609	<i>a</i> 610	<i>a</i> 611	<i>a</i> 612	<i>a</i> 613	<i>a</i> 614	<i>a</i> 617	<i>b</i> 618
<i>a</i> 601	0	1.297	2.287	3.288	3.654	3.366	3.292	3.021	2.475	1.175	1.930	1.805	1.907	3.941	4.343
<i>a</i> 602	1.297	0	1.187	2.562	2.684	2.542	2.110	1.777	1.609	1.563	1.703	1.935	2.496	2.684	3.209
<i>a</i> 603	2.287	1.187	0	1.908	1.743	1.494	1.686	0.893	1.781	2.414	2.078	1.926	2.772	1.751	2.807
<i>a</i> 604	3.288	2.562	1.908	0	0.866	1.215	1.896	1.921	1.839	2.741	1.833	2.178	2.735	2.640	2.530
<i>b</i> 606	3.654	2.684	1.743	0.866	0	0.934	1.605	1.451	2.075	3.281	2.448	2.658	3.381	1.907	2.192
<i>b</i> 607	3.366	2.542	1.494	1.215	0.934	0	2.216	1.627	2.490	3.239	2.565	2.118	2.948	2.093	3.026
<i>b</i> 608	3.292	2.110	1.686	1.896	1.605	2.216	0	1.046	1.174	2.877	2.236	3.155	3.794	1.667	1.142
<i>a</i> 609	3.021	1.777	0.893	1.921	1.451	1.627	1.046	0	1.723	2.954	2.448	2.715	3.526	1.023	2.062
<i>a</i> 610	2.475	1.609	1.781	1.839	2.075	2.490	1.174	1.723	0	1.797	1.186	2.567	2.980	2.652	1.973
<i>a</i> 611	1.175	1.563	2.414	2.741	3.281	3.239	2.877	2.954	1.797	0	0.989	1.888	1.802	3.968	3.771
<i>a</i> 612	1.930	1.703	2.078	1.833	2.448	2.565	2.236	2.448	1.186	0.989	0	1.787	1.918	3.461	3.054
<i>a</i> 613	1.805	1.935	1.926	2.178	2.658	2.118	3.155	2.715	2.567	1.888	1.787	0	0.940	3.592	4.186
<i>a</i> 614	1.907	2.496	2.772	2.735	3.381	2.948	3.794	3.526	2.980	1.802	1.918	0.940	0	4.459	4.757
<i>a</i> 617	3.941	2.684	1.751	2.640	1.907	2.093	1.667	1.023	2.652	3.968	3.461	3.592	4.459	0	2.264
<i>b</i> 618	4.343	3.209	2.807	2.530	2.192	3.026	1.142	2.062	1.973	3.771	3.054	4.186	4.757	2.264	0

Table S3. Couplings (cm⁻¹) between the pigments 601-618, calculated in the point-dipole approximation.

	<i>a</i> 601	<i>a</i> 602	<i>a</i> 603	<i>a</i> 604	<i>b</i> 606	<i>b</i> 607	<i>b</i> 608	<i>a</i> 609	<i>a</i> 610	<i>a</i> 611	<i>a</i> 612	<i>a</i> 613	<i>a</i> 614	<i>a</i> 617	<i>b</i> 618
<i>a</i> 601	0	-43.71	11.18	2.67	2.23	3.16	-2.19	-4.77	1.24	-50.36	3.73	5.55	-9.46	0.98	0.32
<i>a</i> 602	-43.71	0	33.03	6.65	6.02	6.36	-8.96	-26.44	-10.32	8.52	16.91	-5.50	2.37	1.81	0.92
<i>a</i> 603	11.18	33.03	0	-5.52	-12.72	1.31	8.16	171.41	14.34	-4.21	-1.64	2.59	-6.83	-11.10	-2.17
<i>a</i> 604	2.67	6.65	-5.52	0	82.60	28.32	-1.00	-7.44	-5.39	-3.17	1.90	0.59	-3.49	4.58	1.75
<i>b</i> 606	2.23	6.02	-12.72	82.60	0	59.16	-3.20	-3.97	-3.30	-2.82	3.27	1.31	-2.21	7.23	-1.47
<i>b</i> 607	3.16	6.36	1.31	28.32	59.16	0	-4.39	-13.13	0.69	-3.02	2.95	0.60	-3.57	2.23	-0.93
<i>b</i> 608	-2.19	-8.96	8.16	-1.00	-3.20	-4.39	0	51.74	50.35	4.35	-0.59	-1.99	1.47	-1.28	23.39
<i>a</i> 609	-4.77	-26.44	171.41	-7.44	-3.97	-13.13	51.74	0	2.76	5.53	-2.80	-3.25	2.84	37.08	7.89
<i>a</i> 610	1.24	-10.32	14.34	-5.39	-3.30	0.69	50.35	2.76	0	-25.37	16.43	7.12	-2.21	2.36	7.17
<i>a</i> 611	-50.36	8.52	-4.21	-3.17	-2.82	-3.02	4.35	5.53	-25.37	0	130.33	-9.49	5.57	-0.48	0.69
<i>a</i> 612	3.73	16.91	-1.64	1.90	3.27	2.95	-0.59	-2.80	16.43	130.33	0	-2.75	2.07	1.30	0.29
<i>a</i> 613	5.55	-5.50	2.59	0.59	1.31	0.60	-1.99	-3.25	7.12	-9.49	-2.75	0	-76.54	-1.04	-0.77
<i>a</i> 614	-9.46	2.37	-6.83	-3.49	-2.21	-3.57	1.47	2.84	-2.21	5.57	2.07	-76.54	0	-0.78	0.05
<i>a</i> 617	0.98	1.81	-11.10	4.58	7.23	2.23	-1.28	37.08	2.36	-0.48	1.30	-1.04	-0.78	0	-1.61
<i>b</i> 618	0.32	0.92	-2.17	1.75	-1.47	-0.93	23.39	7.89	7.17	0.69	0.29	-0.77	0.05	-1.61	0

4. Exciton-CT coupling

Charge separation can occur within any tightly packed pair of Chls. The best candidate is the *a*603-609 dimer with shortest pigment-pigment spacing in the Chls *a* region (and biggest exciton coupling). In addition, the red spectral forms (reflecting a mixing with the CT state) are changed dramatically upon mutation affecting the environment of these two Chls. Therefore, we suppose that the CT state corresponds to a charge separation within the *a*603-609 dimer. The coupling with CT in Lhca4 is not known exactly. Modeling of other complexes gave different values.

1. In bacterial RC (BRC) the coupling with primary CT has been estimated as 25-35 cm^{-1} based on molecular dynamics simulation (Warshel and Parson, 2001; Sumi, 1997). A similar value of 40 cm^{-1} is needed to reproduce the dynamics of coherent charge separation in the BRC (Novoderezhkin et al., 2004b). Notice that such couplings produce no sizable borrowing of dipole strength by the CT, that is separated from the excited states by a relatively big energy gap. As a result no red shoulder of the absorption was observed in BRC.

2. In PSII-RC a mixing with primary CT is stronger, i.e. the CT state borrows about 0.3 of the monomeric Chl *a* dipole strength, producing a discernable red shoulder of the absorption. The coupling to CT is estimated in the 45-70 cm^{-1} range according to structure-based calculations (Abramavicius and Mukamel, 2010) and modeling of the kinetics (Novoderezhkin et al., 2011).

3. In Lhca4 the CT borrows about 0.9 of the monomeric Chl *a* dipole strength, meaning that the exciton-CT mixing is very strong. In order to reproduce the spectral consequences of such a mixing we have to suppose a larger exciton-CT coupling. We have checked values from 50 to 200 cm^{-1} . At small couplings it is not possible to reproduce the amplitude of the red tail of OD and of the red SA peaks (because these amplitudes are determined by the dipole strength borrowed by the CT). The OD/SA amplitudes can be increased by shifting the CT energy closer to the energy of the excited states. This will produce the strong exciton-CT mixing, but the position of the FL peak in this case (as well as the position of the red bands of SA) will be too close to the excited state manifold. We have found that the huge red shift of FL can only be reproduced when the energy of CT is shifted to the red. Due to the energy gap between the CT and exciton states, the lowest (mixed exciton-CT) state is predominantly localized at CT in such configuration. The localized CT state is characterized by a bigger reorganization shift (as compared to more mixed (and more delocalized) exciton-CT states in an isoenergetic configuration). This produces further red shifting of the FL peak (and the red SA bands). This way we can reproduce both (i) the OD tail and the SA amplitudes on the red, and (ii) the red shift of the FL and the red SA bands. When we move the CT energy to the red we also have to increase the coupling value (to obtain the necessary mixing of the exciton and CT states). For each value of the CT energy there is some optimal value of coupling. The best fit of the spectra was obtained for a coupling of 150 cm^{-1} and the CT energy shifted by 160 cm^{-1} from the red-most *a*603 site. Notice that other site energies are not so sensitive to the *a*603-609 coupling to CT.

5. Coupling to phonons and slow conformational motion

Parameters of the Brownian oscillator (Eqs S4), including the number of vibrational modes, their frequencies, couplings and damping constants, as well as the parameters of the low-frequency overdamped part can be taken from experimental data (fluorescence line narrowing) and adjusted from the quantitative fit of the spectra, including low-temperature FL, where one can see separately the low-frequency peak and each vibrational component (or at least main groups of the most intense vibrations). We have demonstrated (Novoderezhkin et al., 2004a) how it looks for the LHCII complex. For modeling of Lhca4 we have taken the same spectral density as for LHCII with some adjustment of the damping constant γ_0 and coupling strength λ_0 for the overdamped part and the total Huang-Rhys *S* factor for the 48 high-frequency vibrations (the *S* factor has been adjusted by uniform scaling of all the couplings to vibrations λ_j , where $j=1-48$). For Chls *a* the thus adjusted values are: $\gamma_0=40 \text{ cm}^{-1}$, $\lambda_0=200 \text{ cm}^{-1}$, $S=0.84$.

It should be noticed that different types of states (i.e. excited states of Chls *a*, Chls *b*, and CT states) are characterized by different couplings to fast (phonons and vibrations) and slow nuclear motion

(conformational changes accounted for by the model of static disorder). In the present study we suppose for simplicity that the shape of the electron-phonon spectral density is the same for all the three states (Chls *a*, Chls *b*, CT), but the couplings (λ_0 , λ_j , where $j=1-48$) are different. The corresponding scaling factors have been determined from the fit of the spectra. More specifically, we have found, that the λ_0 and λ_j values determined for Chls *a* should be multiplied by 0.8, and 3.2 for Chls *b*, and CT, respectively. Similarly, the disorder values are different for the Chls *a*, Chls *b*, and CT states and treated as free parameters that should be determined from the fit. In this way we have obtained the disorder value of $\sigma=96$, 67, and 144 cm^{-1} (FWHM) for Chls *a*, Chls *b*, and CT states, respectively.

Our modeling confirms a commonly used assumption that the CT states are more strongly coupled to the environmental degrees of freedom due to an additional Coulomb term (appearing due to the huge static dipole interacting with the surroundings) (Barter et al., 2003; Renger, 2004; Vaitekonis et al., 2005; Mančal et al., 2006; Novoderezhkin et al., 2007). In our fit the coupling to phonons and the disorder value for CT are increased by a factor of 3.2 and 1.5, respectively. Without such scaling it is impossible to explain the red shift and broadening of FL and the shape of SA.

6. Evolutionary-based search

To extract the site energies from the simultaneous fit of the spectra we use an evolutionary-based search. The best results have been obtained with a scheme using simultaneous random mutations of the site energies within strongly coupled clusters (i.e. we mutate simultaneously the three energies of the pigments within the *a*610-611-612 trimer, then we mutate the *a*602-603-609-CT block, then the monomeric *a*604 site, and so on...). The algorithm minimizes the square of the deviation from the experimental spectra. This deviation is calculated for a number of discrete points, i.e. 30-50 (depending on the spectrum) non-equally spaced points, covering the region near the maxima (with smaller step) and the tails (with larger step). The weights of the deviations are 7, 7, 4, and 2 for the OD, LD, FL, and SA spectra, respectively.

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