Electronic supplementary information (ESI) for

Excitation energy equilibration in trimeric LHCII complex involves unusual pathways

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S1. Standard Redfield theory

We consider molecular aggregate containing N molecules. The one-exciton Hamiltonian in the site representation is:

$$H=\sum_{j=1}^{N}\omega_j|j\rangle\langle j|+\sum_{j\neq j'}^{N}M_{jj'}|j\rangle\langle j'| \tag{S1}$$

where $\omega_j=\omega_j^0+\lambda_j$ is the energy of the Franck-Condon transition of the j-th site (including the zero-phonon energy ω_j^0 and reorganization energy λ_j), $M_{jj'}$ is the interaction energy between the j-th and j'-th sites.

Supposing that the mixing of the electronic excitations is not dependent on the phonon coordinates, it is possible to switch to the exciton representation by diagonalization of the electronic Hamiltonian (S1). This leads us to the wavefunctions c_j^k giving the participation of the j-th site in the k-th exciton state and to the new set of energies $\omega_k=\omega_k^0+\lambda_{kkkk}$ corresponding to transitions from the ground to the k-th exciton state (where transition frequencies ω_k^0 correspond to the zero-phonon lines in the exciton representation and λ_{kkkk} is the reorganization energy of the k-th exciton state). The excited-state dynamics is then given by equation for the density matrix in the exciton representation:

$$\frac{d}{dt}p_{kk'}=-i\omega_{kk'}^{0}p_{kk'}-\sum_{pp'}R_{kk'pp'}p_{pp'} \tag{S2}$$

with the Redfield relaxation tensor [1,2]:

$$\begin{aligned}R_{kk'pp'}&=-Y_{pkp'k'}-Y^{*}_{p'k'pk}+\delta_{p'k'}\sum_{s}Y_{pssk}+\delta_{pk}\sum_{s}Y^{*}_{p'ssk'}\\ Y_{kk'k''k'''}&=\int_{0}^{\infty}dt\cdot e^{i\omega_{kk'}^{0}t}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}C_{kk'k''k'''}(\omega)\ \left[\coth\tfrac{\omega}{2\theta}\cos\omega t-i\sin\omega t\right]\end{aligned} \tag{S3}$$

where indices k, p, s number the exciton eigenstates, p_{kk} and $p_{kk'}$ are the density matrix elements corresponding to populations and coherences in the exciton representation; $\omega_{kk'}^0=\omega_k^0-\omega_{k'}^0$ is the energy gap between the two states, $C_{kk'k''k'''}$ is the spectral density of electron-phonon coupling in the exciton representation:

$$C_{kk'k''k'''}(\omega)=\sum_{j}c_j^{k}c_j^{k'}c_j^{k''}c_j^{k'''}C_j(\omega) \tag{S4}$$

where $C_j(\omega)$ is the spectral density in the site-representation. Notice that the Redfield equation can include arbitrary spectral density $C_j(\omega)$ and arbitrary temperatures. Initial conditions corresponding to excitation of the j-th site are $p_{kk'}=c_j^k p_{jj} c_j^{k'}$. Notice that initial localization at one site corresponds to coherent excitation of several exciton states (by creating populations p_{kk} together with the coherences $p_{kk'}$). After calculating the evolution of the exciton populations p_{kk} and coherences $p_{kk'}$ according to Eq. (S2) we can switch back to the site representations to obtain the kinetics of the site populations $p_{ii}=c_i^k p_{kk'} c_i^{k'}$ and site coherences $p_{ij}=c_i^k p_{kk'} c_j^{k'}$.

In Eq. (S2) the phonons do not perturb the exciton wavefunctions, but induce transfers between the exciton eigenstates. The rates of the transfers between one-exciton populations, between coherences, and population-coherences transfers (S3) are calculated supposing a weak coupling to phonons and treating the exciton-phonon interaction as a perturbation.

Sometimes the so-called secular approximation is used, keeping only the $R_{kk'pp'}$ elements with $\omega_{kk'}^0-\omega_{pp'}^0=0$. Notice that the dynamics of populations and coherences can change dramatically when switching from the full to secular $R_{kk'pp'}$ tensor.

S2. Modified Redfield theory

The modified Redfield theory [3] is restricted to one-exciton population transfers, but the relaxation tensor is calculated supposing a more realistic description of the exciton-phonon coupling. More specifically, the diagonal (in the exciton representation) part of exciton-phonon coupling is taken into account non-perturbatively, thus giving a realistic line shape for the exciton levels. The off-diagonal part (responsible for transitions between the exciton states) is treated as a perturbation. The exciton wavefunctions are still independent of the phonon coordinates. Moreover, the phonons are supposed to remain equilibrated during the electronic energy transfer. In the Markovian limit (used in our study) the k'→k population transfers are given by the tensor $R_{kkk'k'}$ [3,4]:

$$
\begin{aligned}
R_{kkk'k'} &= 2\,\mathrm{Re}\int_0^\infty dt\, A_k(t)\, F_{k'}^*(t)\, V_{kk'}(t) \\
A_k(t) &= \exp\left\{ i(\omega_k^0+\lambda_{kkkk})t - g_{kkkk}(t) \right\} \\
F_{k'}(t) &= \exp\left\{ i(\omega_{k'}^0-\lambda_{k'k'k'k'})t - g_{k'k'k'k'}^*(t) \right\}
\end{aligned}
\qquad \text{(S5)}
$$

$$
\begin{aligned}
V_{kk'}(t) &= \exp(2g_{k'k'kk}(t) + 2i\lambda_{k'k'kk}t)\times \\
&\times\Big[g^{(2)}_{kk'k'k}(t) - \left\{ g^{(1)}_{k'kk'k'}(t) - g^{(1)}_{k'kkk}(t) + 2i\lambda_{k'kk'k'} \right\}\times \\
&\qquad \times \left\{ g^{(1)}_{k'k'kk'}(t) - g^{(1)}_{kkkk'}(t) + 2i\lambda_{k'k'kk'} \right\}\Big] \\
g^{(1)} &= \frac{dg}{dt};\quad g^{(2)} = \frac{d^2g}{dt^2};
\end{aligned}
$$

where F(t) and A(t) are line-shape functions corresponding to fluorescence of the donor state and absorption of the acceptor, respectively, while V describes the interaction between donor and acceptor, ω_k^0 is the zero-phonon energy of the k-th exciton state. Other quantities are related to the exciton-phonon spectral density in the site representation $C_j(\omega)$:

$$
\begin{aligned}
g_{kk'k''k'''}(t) &= \sum_j c_j^k c_j^{k'} c_j^{k''} c_j^{k'''} g_j(t) \\
\lambda_{kk'k''k'''}(t) &= \sum_j c_j^k c_j^{k'} c_j^{k''} c_j^{k'''} \lambda_j \\
g_j(t) &= -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega^2} C_j(\omega)\left[(\cos\omega t - 1)\coth\tfrac{\omega}{2\theta} - i(\sin\omega t - \omega t) \right] \\
\lambda_j &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega} C_j(\omega)
\end{aligned}
\qquad \text{(S6)}
$$

where $g_j(t)$ and λ_j are line-broadening function and reorganization energy of the j-th diabatic state.

If the donor and acceptor states are localized at the j-th and i-th sites (i.e. $c_j^{k'}=1$ and $c_i^k=1$) then the transfer between them is given by the Förster formula, that can be obtained from (S5) by replacing the interaction term by [4,5]

$$V_{kk'} = \left|M_{ij}\right|^2 \tag{S7}$$

where M_{ij} is the interaction energy corresponding to a weak coupling between the localized sites i and j. Switching to the Fourier-transforms of F(t) and A(t) we can rewrite the integral in a form of donor-acceptor spectral overlap [6]. The standard Förster formula can be generalized to the case of energy transfer between two weakly connected clusters [5,7]. The rate of energy transfer from the k'-th exciton state of one cluster to the k-th state of the other cluster is given by (S5) with the interaction term:

$$V_{kk'} = \left|\sum_{i,j} c_i^k M_{ij} c_j^{k'}\right|^2 \tag{S8}$$

where i and j designate molecules belonging to different clusters. In this generalized Förster formula, the donor and acceptor states k' and k can have an arbitrary degree of delocalization (corresponding to arbitrarily strong excitonic interactions within each cluster), but the inter-cluster interactions M_{ij} are supposed to be weak. In the combined Redfield-Förster approach [5,7-9] the relaxation dynamics within strongly coupled clusters is calculated with the modified Redfield theory, whereas transfers between these clusters (with weak inter-clusters couplings) are modeled by the generalized Förster theory.

S3. Coherent modified Redfield theory

The coherent modified Redfield (cmR) approach [10-12] is a secular master equation describing the dynamics of the one-exciton populations ρ_{kk} and the decay of the coherences $\rho_{kk'}$ between the exciton states. Non-secular terms, i.e. transfers between coherences and transfers between populations and coherences are not included. As in the original modified Redfield model [3] the diagonal exciton-phonon coupling is included explicitly, whereas the off-diagonal phonon-induced fluctuations (inducing relaxation between the exciton states) are treated perturbatively. Population dynamics is given by the same equation as in modified Redfield (S5), whereas the decay of the coherences is given by [12]:

$$R_{kk'kk'} = \tfrac{1}{2} R_{kkkk} + \tfrac{1}{2} R_{k'k'k'k'} + \Gamma_{kk'}; \quad \Gamma_{kk'}(t) = \sum_j \left[(c_j^k)^2 - (c_j^{k'})^2\right]^2 (g_j^{(1)}(t) + i\lambda_j) \tag{S9}$$

where R_{kkkk} is the inverse lifetime of the k-th exciton state (determined by the sum of the k→k' relaxation rates $R_{k'k'kk}$), $\Gamma_{kk'}$ is pure dephasing. In the Markovian approximation the time-independent dephasing term is (bearing in mind that $\mathrm{Im}\{g^{(1)}(\infty)\} = -\lambda$):

$$\Gamma_{kk'}(\infty) = \sum_j \left[(c_j^k)^2 - (c_j^{k'})^2\right]^2 \mathrm{Re}\left\{g_j^{(1)}(\infty)\right\} \tag{S10}$$

This way a coherent modified Redfield theory describes the transfers between the one-exciton populations (S5) together with the decay of the coherences (S9). Unfortunately, the non-secular terms, i.e. transfers between coherences as well as transfers between populations and coherences are not included. These terms are important to describe transfers between the weakly coupled and isoenergetic sites, where non-secular transfers maintain long-lived coherences between the exciton (delocalized) eigenstates. These coherences keep the excitation localized, whereas in the secular approximation (where coherences quickly decay without being 're-pumped' from the populations) initially localized excitations exhibit rather fast delocalization between the donor and acceptor states. In the site representation this looks like unrealistically fast energy transfer [13]. The cmR theory suffers from such a 'resonant artifact' that is also present in the original modified Redfield (where the coherences are not included at all). To circumvent it, the cmR can be combined with generalized Förster theory, or with the small polaron quantum master equation [12]. In such combined approaches the most questionable point is how to determine the crossover between the two energy transfer regimes. The simplest way is to split the whole systems into compartments with the exciton couplings $M_{jj'}$ exceeding some critical value, M_c [5,7]. Then the dynamics within the clusters with $M_{jj'}>M_c$ can be described with the Redfield theory, whereas the transfers between these clusters (with inter-cluster couplings $M_{jj'}<M_c$) are treated with the generalized Förster theory. The critical value M_c can be chosen intuitively [5,7,14-19] or by comparing the results with those of exact methods, like hierarchical equation of motion (HEOM) [13,20-23].

S4. Scaled hierarchical equation with low-temperature corrections

The hierarchical equation of motion (HEOM) is restricted to some special forms of the spectral density. We use the spectral density in the form of an overdamped Brownian oscillator (with reorganization energy λ_j and damping constant γ_j):

$$C_j(\omega) = 2\lambda_j \frac{\omega\gamma_j}{\omega^2 + \gamma_j^2} \tag{S11}$$

In this case the scaled HEOM for the reduced density operator is [24]:

$$\begin{gathered}\frac{d}{dt}\sigma^n = -(iH^\times + G + \sum_{j=1}^{N} S_j V_j^\times V_j^\times)\sigma^n - i\sum_{j=1}^{N}\sum_{k=0}^{K}(L_{jk}V_j^\times \sigma^{n_{jk}^+} + G_{jk}V_j\sigma^{n_{jk}^-} - \sigma^{n_{jk}^-}V_j G_{jk}^*) \\ G = \sum_{j=1}^{N}\sum_{k=0}^{K} n_{jk}\nu_{jk}; \quad S_j = \sum_{k=K+1}^{\infty}\frac{c_{jk}}{\nu_{jk}}; \quad L_{jk} = \sqrt{(n_{jk}+1)\left|c_{jk}\right|}; \quad G_{jk} = \sqrt{\frac{n_{jk}}{\left|c_{jk}\right|}}\,c_{jk}; \\ c_{j0} = \lambda_j\gamma_j(-i + \cot\frac{\gamma_j}{2\theta}); \quad \nu_{j0} = \gamma_j; \qquad c_{jk} = \frac{4\theta\lambda_j\gamma_j\nu_{jk}}{\nu_{jk}^2 - \gamma_j^2}; \quad \nu_{jk} = 2\pi k\theta; \quad (k \geq 1)\end{gathered} \tag{S12}$$

where σ^n denote auxiliary operators dependent on the set of integers describing the state of the phonon bath of the sites from j=1 to N; $n=\{n_{10},..n_{1K},..n_{jk},..n_{N0},..n_{NK}\}$; $n_{jk}^{\pm}=\{\ldots\ n_{jk}\pm1\ldots\}$; the index k (not to be confused with the index k labeling the exciton states in previous sections!) numbers the low-temperature correction terms from k=0 to K; $\theta=k_BT$, where k_B is the Boltzmann constant, T is the temperature. The auxiliary operators σ^n at $n=\{0,0,\ldots0\}$ are equal to the reduced density operator ρ. Here $V^\times\sigma$ denotes a commutator, i.e. $V^\times\sigma = V\sigma-\sigma V$, where $V_j=|j\rangle\langle j|$. Notice that Eq. (S12) implies that the phonons associated with different sites are uncorrelated. The dynamics of the one-exciton populations σ_{ii} and coherences σ_{ij} (in the site representation) is given by:

$$\begin{aligned}\frac{d}{dt}\sigma_{ij}^n &= (-i\omega_{ij} - (1-\delta_{ij})(S_i + S_j) - G)\sigma_{ij}^n - i\sum_{s=1}^{N}(M_{is}\sigma_{sj}^n - \sigma_{is}^n M_{sj}) - \\ &\quad -i\sum_{k=0}^{K}(L_{ik}\sigma_{ij}^{n_{ik}^+} - \sigma_{ij}^{n_{jk}^+}L_{jk} + G_{ik}\sigma_{ij}^{n_{ik}^-} - \sigma_{ij}^{n_{jk}^-}G_{jk}^*)\end{aligned} \tag{S13}$$

with $\omega_{ij}=\omega_{i0}-\omega_{j0}$., and with some initial conditions for σ_{ij} describing the state of the system after impulsive excitation. For example, excitation of the j-th site corresponds to $\sigma_{ii}^n=1$ for $n=\{0,0,\ldots0\}$ and $\sigma_{ii}^n=0$ for other n sets. If the sum of n_{jk} exceeds N_c, then the terms with G, G_{ik}, and L_{ik} in Eqs. (S12) and (S13) are set to zero [25]. The depth of the hierarchy N_c and the number of the Matsubara frequencies K should be chosen in order to get converging results. The scaled HEOM gives converging results already at small cutoff values N_c. In our numerical examples one can restrict to N_c=3-4 (for N_c>4 there are no visible changes in the kinetics). At room temperature there is only small difference between the K=0 and K=1 cases (where K is the number of temperature correction terms). Therefore we calculate the scaled HEOM kinetics with N_c=3, K=0.

S5. Model of trimeric LHCII complex

We use the exciton model of LHCII trimer developed in ref. 16. Table S1 shows the pigment-pigment couplings (the same as in ref.16). Table S2 shows the site energies for the first subunit (we suppose the same sets of the unperturbed site energies for the second and third subunits). Notice that we formally include the b601' site to the first subunit (as in ref. 16).

Table S1. Interaction energies M_{nm} (cm^{-1}) for the trimeric LHCII complex, calculated in the point-dipole approximation (data taken from ref.16).

	a602	a603	a610	a611	a612	b608	b609	b601'	a613	a614	a604	b605	b606	b607
a602	0	38.11	-11.39	9.69	15.83	-5.84	-19.25	-0.35	-4.96	0.69	6.42	-0.71	5.60	7.13
a603	38.11	0	12.97	-2.70	-0.76	6.72	96.66	-0.71	2.68	-6.70	-3.28	1.13	-8.89	1.23
a610	-11.39	12.97	0	-24.96	23.10	61.97	3.86	-4.20	7.21	-1.55	-4.18	1.61	-3.28	-0.14
a611	9.69	-2.70	-24.96	0	126.92	4.35	4.30	-0.88	-6.15	4.55	-3.80	1.33	-2.52	-2.78
a612	15.83	-0.76	23.10	126.92	0	-1.08	-2.57	1.41	-0.47	-0.18	4.67	-2.85	3.10	3.07
b608	-5.84	6.72	61.97	4.35	-1.08	0	36.07	5.82	-2.01	1.30	-2.76	-5.13	-4.99	-4.43
b609	-19.25	96.66	3.86	4.30	-2.57	36.07	0	38.15	-2.92	2.33	-7.28	-0.77	-0.16	-11.99
b601'	-0.35	-0.71	-4.20	-0.88	1.41	5.82	38.15	0	0.90	0.17	2.69	-2.26	2.72	0.30
a613	-4.96	2.68	7.21	-6.15	-0.47	-2.01	-2.92	0.90	0	-50.22	2.12	-1.40	1.47	2.20
a614	0.69	-6.70	-1.55	4.55	-0.18	1.30	2.33	0.17	-50.22	0	-3.42	0.37	-2.16	-3.25
a604	6.42	-3.28	-4.18	-3.80	4.67	-2.76	-7.28	2.69	2.12	-3.42	0	3.35	104.56	35.93
b605	-0.71	1.13	1.61	1.33	-2.85	-5.13	-0.77	-2.26	-1.40	0.37	3.35	0	29.71	-4.47
b606	5.60	-8.89	-3.28	-2.52	3.10	-4.99	-0.16	2.72	1.47	-2.16	104.56	29.71	0	59.38
b607	7.13	1.23	-0.14	-2.78	3.07	-4.43	-11.99	0.30	2.20	-3.25	35.93	-4.47	59.38	0
a602'	1.11	8.14	2.95	0.55	-0.69	0.08	-10.66	49.64	-1.20	-0.86	-0.90	0.66	-0.82	0.53
a603'	5.22	-6.53	-0.91	-1.21	1.29	-0.54	0.23	-5.89	-0.48	-0.91	2.56	-0.26	2.80	3.18
a610'	0.76	-2.05	-0.68	-0.36	0.51	0.54	2.25	-5.95	0.07	-0.01	0.54	0.06	0.25	-0.20
a611'	-0.51	-0.15	-1.13	-0.24	0.57	2.70	4.63	24.89	0.45	0.29	0.27	-0.32	-0.78	-0.85
a612'	-0.51	2.40	1.14	0.42	-0.29	-0.61	-3.19	9.13	-0.66	-0.07	-0.67	0.48	-0.36	-0.43
b608'	-1.15	1.32	0.50	0.44	-0.11	0.40	-0.23	2.78	-0.17	0.38	-0.71	0.22	-0.67	-0.66
b609'	-2.33	2.33	0.68	0.71	-0.41	0.42	-0.34	3.79	-0.17	0.43	-1.05	0.18	-0.99	-0.94
b601"	0.22	-1.45	-0.34	-0.09	0.35	0.46	0.89	-0.43	0.23	0.73	-0.25	0.16	-0.34	-0.59
a613'	-0.44	-4.36	-1.19	0.22	-0.93	0.38	5.24	-10.79	2.00	0.97	-1.08	-0.97	-0.89	8.18
a614'	-2.51	4.15	0.70	0.81	-0.76	0.74	-4.57	3.59	0.49	1.11	-3.91	3.43	-5.63	0.73
a604'	1.15	-0.50	-0.19	-0.30	-0.01	-0.59	-0.26	-2.51	-0.25	-0.68	0.87	-0.49	1.07	1.34
b605'	-0.34	0.50	0.22	0.17	-0.04	0.04	-0.23	0.77	-0.22	0.12	-0.29	0.07	-0.20	-0.20
b606'	1.17	-0.41	-0.23	-0.36	0.10	-0.41	-0.12	-1.87	-0.23	-0.66	0.80	-0.24	0.82	0.88
b607'	1.82	-0.97	-0.43	-0.56	0.20	-0.47	-0.00	-2.49	0.22	-0.68	1.21	-0.34	1.20	1.51
a602"	1.11	5.22	0.76	-0.51	-0.51	-1.15	-2.33	0.22	-0.44	-2.51	1.15	-0.34	1.17	1.82
a603"	8.14	-6.53	-2.05	-0.15	2.40	1.32	2.33	-1.45	-4.36	4.15	-0.50	0.50	-0.41	-0.97
a610"	2.95	-0.91	-0.68	-1.13	1.14	0.50	0.68	-0.34	-1.19	0.70	-0.19	0.22	-0.23	-0.43
a611"	0.55	-1.21	-0.36	-0.24	0.42	0.44	0.71	-0.09	0.22	0.81	-0.30	0.17	-0.36	-0.56
a612"	-0.69	1.29	0.51	0.57	-0.29	-0.11	-0.41	0.35	-0.93	-0.76	-0.01	-0.04	0.10	0.20
b608"	0.08	-0.54	0.54	2.70	-0.61	0.40	0.42	0.46	0.38	0.74	-0.59	0.04	-0.41	-0.47
b609"	-10.66	0.23	2.25	4.63	-3.19	-0.23	-0.34	0.89	5.24	-4.57	-0.26	-0.23	-0.12	-0.00
b601	49.64	-5.89	-5.95	24.89	9.13	2.78	3.79	-0.43	-10.79	3.59	-2.51	0.77	-1.87	-2.49
a613"	-1.20	-0.48	0.07	0.45	-0.66	-0.17	-0.17	0.23	2.00	0.49	-0.25	-0.22	-0.23	0.22
a614"	-0.86	-0.91	-0.01	0.29	-0.07	0.38	0.43	0.73	0.97	1.11	-0.68	0.12	-0.66	-0.68
a604"	-0.90	2.56	0.54	0.27	-0.67	-0.71	-1.05	-0.25	-1.08	-3.91	0.87	-0.29	0.80	1.21
b605"	0.66	-0.26	0.06	-0.32	0.48	0.22	0.18	0.16	-0.97	3.43	-0.49	0.07	-0.24	-0.34
b606"	-0.82	2.80	0.25	-0.78	-0.36	-0.67	-0.99	-0.34	-0.89	-5.63	1.07	-0.20	0.82	1.20
b607"	0.53	3.18	-0.20	-0.85	-0.43	-0.66	-0.94	-0.59	8.18	0.73	1.34	-0.20	0.88	1.51

Table S2. The site energies ω_j (cm^{-1}) corresponding to purely electronic transitions, i.e. not including a reorganization energy shift.

	Site energies
a602	15097
a603	15227
a610	15013
a611	15055
a612	15037
b608	15628
b609	15586
b601'	15754
a613	15115
a614	15204
a604	15400
b605	15544
b606	15716
b607	15577

The data from Tables S1 and S2 is enough to build the one-exciton Hamiltonian (S1). Switching to the exciton representation (by diagonalization of (S1)) gives us the exciton energies energies ω_k and the wavefunctions c_j^k allowing a calculation of the Redfield relaxation rates (S3), (S5) or (S9). The Redfield-Förster approach implies diagonalization of Hamiltonian and calculation of the Redfield relaxation tensor for each compartment. The transfers between compartments are given by generalized Förster rates (given by (S5) and (S8)). The HEOM kinetics (S12) are calculated in the site representation. In our modeling both the Redfield and HEOM kinetics are calculated using the electron-phonon spectral density (S11) with λ_j=300 cm^{-1} and γ_j=500 cm^{-1}. (where the λ_j and γ_j values are supposed to be the same for all the sites). The kinetics are calculated for room temperature (T=293K). Notice that the site energies in Table S2 are different from the original energy set obtained in ref. 16. The original energies emerged from the Redfield modeling with realistic spectral density, whereas in the present study we use a simplified spectral density (S11) enabling us to use the HEOM equation (S12). This spectral density gives a reduced reorganization shift that can be compensated by some uniform shifting of the site energies (as explained in ref. 26). In Table S2 we show the thus adjusted (shifted) site energies.

The calculation steps for the Redfield approach include:

(i) building of one-exciton Hamiltonian (S1);
(ii) diagonalization of Hamiltonian;
(iii) calculation of relaxation tensor (S3, S5, or S9);
(iv) solving of the Redfield equation (S2).

The calculation steps for the Redfield-Förster approach include:

(i) diagonalization of Hamiltonian and calculation of relaxation tensor for each compartment;
(ii) calculation of generalized Förster rates for the transfers between compartments;
(iii) solving of equation (S2), where the k-th and p-th states may belong to the same or to different compartments (transfers between compartments are incoherent (i.e. $p_{kk'} = \delta_{kk'}$ and $p_{pp'} = \delta_{pp'}$) with the R_{kkpp} elements corresponding to the p→k generalized Förster rates).

The calculation steps for the HEOM approach include:

(i) building of one-exciton Hamiltonian (S1);
(ii) solving of hierarchical equation (S13) in the site representation .

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