

Electronic supplementary information (ESI) for Multiexciton spectra of molecular aggregates: application to photosynthetic antenna complexes

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S1. The structure of Hamiltonian for N=4

In the case of N=4 the one-exciton Hamiltonian in the site representation (i.e. in the basis of the wavefunctions $|n\rangle$ localized at molecules $n=1, 2, 3,$ and 4) is:

H_1	$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$
$ 1\rangle$	E_1	M_{12}	M_{13}	M_{14}
$ 2\rangle$	M_{12}	E_2	M_{23}	M_{24}
$ 3\rangle$	M_{13}	M_{23}	E_3	M_{34}
$ 4\rangle$	M_{14}	M_{24}	M_{34}	E_4

The number of elementary two-exciton states (denoted as $|nm\rangle=|1,2\rangle, |1,3\rangle, \dots$ etc., where $m>n$) is $N(N-1)/2!$, i.e. 6 for N=4. The two-exciton Hamiltonian in this basis is:

H_2	$ 1,2\rangle$	$ 1,3\rangle$	$ 1,4\rangle$	$ 2,3\rangle$	$ 2,4\rangle$	$ 3,4\rangle$
$ 1,2\rangle$	E_1+E_2	M_{23}	M_{24}	M_{13}	M_{14}	0
$ 1,3\rangle$	M_{23}	E_1+E_3	M_{34}	M_{12}	0	M_{14}
$ 1,4\rangle$	M_{24}	M_{34}	E_1+E_4	0	M_{12}	M_{13}
$ 2,3\rangle$	M_{13}	M_{12}	0	E_2+E_3	M_{34}	M_{24}
$ 2,4\rangle$	M_{14}	0	M_{12}	M_{34}	E_2+E_4	M_{23}
$ 3,4\rangle$	0	M_{14}	M_{13}	M_{24}	M_{23}	E_3+E_4

The off-diagonal matrix elements are expressed through the interaction energies between the pairs of molecular, i.e. the same values as appear in the one-exciton Hamiltonian. For example, interaction between the states $|1,2\rangle$ and $|1,3\rangle$ is M_{23} corresponding to jump of one excitation from site 2 to 3 (whereas second excitation keep staying at $n=1$). Notice that elementary excitation $|nm\rangle$ is the same as $|mn\rangle$, so it is convenient to consider only $|nm\rangle$ with $m>n$. In such notations the interaction between in the states $|2,3\rangle$ and $|3,4\rangle$ is M_{24} corresponding to jump from $n=2$ to 4 (the second excitation stays at $n=3$). Similarly, the three-exciton Hamiltonian (in the basis of $|nmp\rangle$ states, where $p>m>n$) is:

H_3	$ 1,2,3\rangle$	$ 1,2,4\rangle$	$ 1,3,4\rangle$	$ 2,3,4\rangle$
$ 1,2,3\rangle$	$E_1+E_2+E_3$	M_{34}	M_{24}	M_{14}
$ 1,2,4\rangle$	M_{34}	$E_1+E_2+E_4$	M_{23}	M_{13}
$ 1,3,4\rangle$	M_{24}	M_{23}	$E_1+E_3+E_4$	M_{12}
$ 2,3,4\rangle$	M_{14}	M_{13}	M_{12}	$E_2+E_3+E_4$

Generally, there are $N(N-1)(N-2)/3!$ three-exciton wavefunctions. For $N=4$ we got 4 states, i.e. their number is less than the number of two-exciton states. But for larger aggregates ($N>5$) the number of three-exciton states increases in proportion to N^3 and significantly exceeds the number of the two-exciton states.

Finally, the four-exciton Hamiltonian in the case of $N=4$ is given by a single state corresponding to excitations of all the four molecules:

H_4	$ 1,2,3,4\rangle$
$ 1,2,3,4\rangle$	$E_1+E_2+E_3+E_4$

S2. The structure of transient absorption for $N=4$

S2.1 Definition of the transient absorption

In this section we illustrate the structure of the transient absorption (TA) signal. For simplicity we consider molecular aggregates made of $N=4$ two-level molecules. In Fig. S1 we show an ensemble of such aggregates (numbering them as $N^{\circ}1$, $N^{\circ}2$, etc.). Each aggregate in the ensemble is characterized by its own conformational state (that determines conformation-induced shifts of the transition energies of its molecules) and by its own orientation with respect to polarization of the pump pulse.

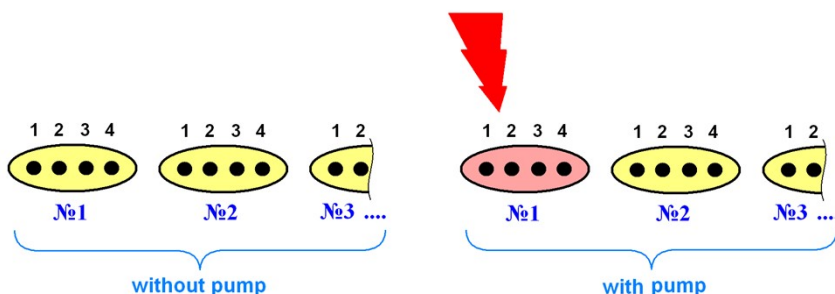


Fig. S1 The scheme illustrating evaluation of the transient absorption for the ensemble of molecular aggregates made of $N=4$ two-level molecules. We suppose that pump pulse creates excitation in the aggregate $N^{\circ}1$.

The TA signal is defined as a difference in absorbance (of the whole ensemble) with the presence of pump pulse and without pump. Absorption of one quantum from the pump can create the excited state within some aggregate. In Fig. S1 we suppose that the aggregate $N^{\circ}1$ is excited. Considering excitations of other aggregates ($N^{\circ}2$, $N^{\circ}3$, etc.) is equivalent to averaging over disorder and orientations (where contributions from individual aggregates should be weighed with the excitation probability for each

aggregate). We show how to do it in next section, but now we restrict to analysis of the TA corresponding to excitation of the aggregate N°1. In this case the TA is equal to $A_{\text{ex}}-A_{\text{g}}$, where A_{ex} is the absorption corresponding to the excited state of the aggregate N°1, whereas A_{g} is the absorption of the same aggregate in the ground (non-excited) state. Contributions from other aggregates (N°2, N°3, etc.) to the total absorption in the presence of pump and without pump are the same and cancel each other.

S2.2 Localized excitations

Let us first consider the $TA=A_{\text{ex}}-A_{\text{g}}$ in the case of localized excitations within the aggregate N°1 (supposing that the 4 molecules within this aggregate are very weakly coupled). Without pump the system is in the ground state, i.e. $|0,0,0,0\rangle$, where zeros indicate the state of the n -th molecule ($n=1-4$) without excitation. The ground-state absorption A_{g} is given by the sum of four transitions with the transition dipoles $\mathbf{d}_1-\mathbf{d}_4$ corresponding to excitation of the n -th molecule. These transitions determine the ground-state bleaching (GSB) of the whole aggregate that contribute to the TA with a negative sign (as indicated in the Table S1). Suppose that the excited state the aggregate is given by excitation localized at the $n=1$ molecule, i.e. $|1,0,0,0\rangle$. Interaction of the probe pulse with this state will produce stimulated emission (SE) to the ground $|0,0,0,0\rangle$, giving negative contribution to the TA, and positive excited-state absorption (ESA) components, corresponding to absorption of the second quantum. The second quantum cannot be absorbed by $n=1$ molecule that is already excited (remind that we consider two-level molecules!). But this second quantum can induce ground-to-excited state transitions from non-excited $n=2-4$ molecules (with the dipoles $\mathbf{d}_2-\mathbf{d}_4$ as indicated for ESA components in the Table 1). Notice that the three ESA components are identical to the three GSB transitions (and have the same dipoles $\mathbf{d}_2-\mathbf{d}_4$ and the same transition energies). It means that the absorption from the excited state is nothing else but modified ground-state absorption. Modification caused by the presence of one excited molecule is reduced to the absence of absorption of this particular molecule. Therefore, the sum of the 8 components contributing to the total TA signal will contain 6 canceled contributions, whereas the remaining two correspond to the bleaching of the $n=1$ molecule and the emission from this molecule. The integrated bleaching of the TA signal is equal to -2 in the units of the monomeric dipole strength.

Table S1. The TA components for $N=4$ in the case of localized excitations. Transition between the states and the corresponding transition dipoles (in the brackets $\{\}$) are indicated for each component, together with its origin (i.e. GSB, SE, or ESA) and the sign (i.e. “+” or “-”).

Non-interacting molecules, localized excitations					
$-A_{\text{g}}$, absorption from the ground state			A_{ex} , absorption from the excited state		
GSB	-	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_1\} \rightarrow 1,0,0,0\rangle$	SE	-	$ 1,0,0,0\rangle \rightarrow \{\mathbf{d}_1\} \rightarrow 0,0,0,0\rangle$
GSB	-	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_2\} \rightarrow 0,1,0,0\rangle$	ESA	+	$ 1,0,0,0\rangle \rightarrow \{\mathbf{d}_2\} \rightarrow 1,1,0,0\rangle$
GSB	-	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_3\} \rightarrow 0,0,1,0\rangle$	ESA	+	$ 1,0,0,0\rangle \rightarrow \{\mathbf{d}_3\} \rightarrow 1,0,1,0\rangle$
GSB	-	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_4\} \rightarrow 0,0,0,1\rangle$	ESA	+	$ 1,0,0,0\rangle \rightarrow \{\mathbf{d}_4\} \rightarrow 1,0,0,1\rangle$

S2.3 Partially delocalized excitations

As another example consider the excited state delocalized over two strongly coupled molecules ($n=1,2$) with other two ($n=3,4$) decoupled from them and localized. The two excited states of the $n=1,2$ dimer are given by a coherent superposition of the $|1,0,0,0\rangle$ and $|0,1,0,0\rangle$ states. The total GSB of these two exciton states will always have the dipole strength equal to the sum of the monomeric dipole strength, i.e. $(\mathbf{d}_1^2+\mathbf{d}_2^2)$. In the case of symmetric dimer with parallel (head-to-tail) dipoles ($\mathbf{d}_1=\mathbf{d}_2=\mathbf{d}$) the higher exciton state is dipole forbidden ($c_1-\mathbf{d}_1-c_2-\mathbf{d}_2=0$) due to symmetry of the wavefunctions, whereas lower state is superradiant with $(c_1+\mathbf{d}_1+c_2+\mathbf{d}_2)^2=2\mathbf{d}^2$ (here we use the wavefunction amplitudes $c_{1,2}^{\pm}$ defined by eqns (2) and (3) - see the main text). The GSB of the localized $n=3$ and 4 molecules has dipole strengths of \mathbf{d}_3^2 and \mathbf{d}_4^2 . Suppose that the excited state corresponds to population of the lower state of the dimer. Then the SE

from this level will have dipole strength $2\mathbf{d}^2$. The ESA from this level corresponds to absorption of the second quantum producing the $|1,1,0,0\rangle$ state from coherent superposition of the $|1,0,0,0\rangle$ and $|0,1,0,0\rangle$ states. The dipole strength of this transition is $(c_1^+\mathbf{d}_2+c_2^+\mathbf{d}_1)^2$ (according to eqn (6) in the main text). Notice that this value is generally different from the ground state absorption to the same level (i.e. $(c_1^+\mathbf{d}_1+c_2^+\mathbf{d}_2)^2$). It means that ESA is a modified ground state absorption containing another linear combination of the same transition dipoles (\mathbf{d}_1 and \mathbf{d}_2). Such modification is more complicated than in the localized case (where we observe just an absence of one excited molecule in ESA). In delocalized case the ESA corresponds to a modified superposition of the two molecules within a dimer (as compared with the initially existing excited state). It can be shown that the energy the ESA transition from the lower exciton state is shifted to the blue with respect to ground-state absorption of this level. In addition to this excited-state absorption within the $n=1,2$ dimer, the ESA of the whole aggregate also contains transitions corresponding to excitation of the localized molecules $n=3$ and 4. Although these transitions occur in the presence of the excitation within the dimer, they do not ‘feel’ the intra-dimer excitation being decoupled from it. Therefore, they give the same spectral lines in ESA as in the GSB corresponding to the same molecules. It means that the last two components in GSB (with the \mathbf{d}_3 and \mathbf{d}_4 dipoles – see the Table S2) are canceled by the two last components in ESA (also with \mathbf{d}_3 and \mathbf{d}_4). After this cancellation there remain the bleaching of the dimer (with the dipole strength of $2\mathbf{d}^2$), SE from the lower exciton state of the dimer (with the $2\mathbf{d}^2$ intensity in the case of symmetric dimer), and the blue-shifted ESA from this level (with the same $2\mathbf{d}^2$ intensity). Altogether, we have the TA signal with integrated bleaching of -2 in the units of the monomeric dipole strength, as in localized case.

Table S2. The TA components for $N=4$ in the case of partially delocalized excitations.

Strongly coupled dimer and two localized molecules		
GSB	–	$ 0,0,0,0\rangle \rightarrow \{c_1^+\mathbf{d}_1+c_2^+\mathbf{d}_2\} \rightarrow c_1^+ 1,0,0,0\rangle + c_2^+ 0,1,0,0\rangle$
GSB	–	$ 0,0,0,0\rangle \rightarrow \{c_1^-\mathbf{d}_1-c_2^-\mathbf{d}_2\} \rightarrow c_1^- 1,0,0,0\rangle - c_2^- 0,1,0,0\rangle$
GSB	–	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_3\} \rightarrow 0,0,1,0\rangle$
GSB	–	$ 0,0,0,0\rangle \rightarrow \{\mathbf{d}_4\} \rightarrow 0,0,0,1\rangle$
SE	–	$c_1^+ 1,0,0,0\rangle + c_2^+ 0,1,0,0\rangle \rightarrow \{c_1^+\mathbf{d}_1+c_2^+\mathbf{d}_2\} \rightarrow 0,0,0,0\rangle$
ESA	+	$c_1^+ 1,0,0,0\rangle + c_2^+ 0,1,0,0\rangle \rightarrow \{c_1^+\mathbf{d}_2+c_2^+\mathbf{d}_1\} \rightarrow 1,1,0,0\rangle$
ESA	+	$c_1^+ 1,0,0,0\rangle + c_2^+ 0,1,0,0\rangle \rightarrow \{\mathbf{d}_3\} \rightarrow c_1^+ 1,0,1,0\rangle + c_2^+ 0,1,1,0\rangle$
ESA	+	$c_1^+ 1,0,0,0\rangle + c_2^+ 0,1,0,0\rangle \rightarrow \{\mathbf{d}_4\} \rightarrow c_1^+ 1,0,0,1\rangle + c_2^+ 0,1,0,1\rangle$

S2.4 Delocalized excitations

If excitations are completely delocalized the GSB will contain transitions to the 4 excited states given by coherent superposition of the $|1,0,0,0\rangle$, $|0,1,0,0\rangle$, $|0,0,1,0\rangle$, and $|0,0,0,1\rangle$ states with the amplitudes c_n^k (obtained from diagonalization of one-exciton Hamiltonian). These 4 excited states will give the SE components corresponding to transition back to the ground state $|0,0,0,0\rangle$ and ESA components corresponding to transitions to the two-exciton states given by superposition of the wavefunctions $|1,1,0,0\rangle$, $|1,0,1,0\rangle$, etc. In delocalized case there is no canceling GSB and ESA contributions. By contrary, ESA consists of the absorption components that is completely modified with respect to the ground-state absorption due to presence of excitations spread over all the molecules. Because the two-level molecule cannot be excited twice, the second exciton (created by absorption of the second quantum) cannot be the same as the already present. It looks like ‘repulsive force’ modifying the structure of the two-exciton states. In particular, they typically become blue-shifted, giving a blue-shifted positive component producing a specific sigmoid shape of the TA.

S2.5 Two-particle TA

At higher energies of the pump the aggregate ($N^{\circ}1$ in our example) can absorb two quanta. The corresponding TA is then different from the TA upon absorption of just one quantum (to distinguish between them we denote these single- and two-particle TA signals as TA_1 and TA_2 , respectively). The TA_2 can be evaluated with the same scheme as used for TA_1 , but the excited state has now two-exciton origin (Fig. S2).

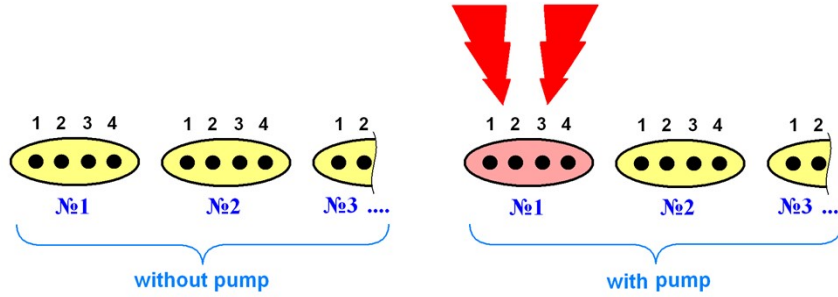


Fig. S2 The scheme explaining the ‘two-particle’ TA corresponding to absorption of the two quanta (as shown by two red arrows). This scheme is the same as for usual (‘single-particle’) TA (shown in Fig. S1), but now the excited state of the aggregate $N^{\circ}1$ is described by a manifold of the two-exciton states.

Comparing Figs. S1 and S2 we conclude that the GSB component given by absorption of non-excited aggregate $N^{\circ}1$ on the left) is the same in both the TA_1 and TA_2 . But the SE_2 and ESA_2 originating from the two-exciton states will be different from SE_1 and ESA_1 . The SE_2 includes emission from the two-to-one-exciton levels (thus resembling the inverted ESA_1 originating from the same transitions). The ESA_2 components correspond to absorption from two- to three-exciton states. The dipole moments of these transitions are given by eqn (9) (see the main text) that contains some linear combination of the ground-state absorption dipoles \mathbf{d}_1 - \mathbf{d}_4 . Notice that in aggregates made of two-level molecules there is no pure ESA (for example due to $S_1 \rightarrow S_2$ transitions as in the case of three-level molecules). It means that the ESA contains no dipoles other than the ground-state $S_0 \rightarrow S_1$ transition dipoles. In this respect the ESA_2 can be considered as ‘modified’ ground-state absorption (similarly to ESA_1). The way how the ground-state absorption is modified (in ESA_1 and ESA_2) is automatically accounted for by the expressions for the transition dipoles \mathbf{d}_{qk} and \mathbf{d}_{rq} (given by eqns (6) and (9)) and by the transition energies $\omega_{qk} = \omega_q - \omega_k$ and $\omega_{rq} = \omega_r - \omega_q$ (obtained using eqns (5) and (8)). These quantities should be then included into the expressions for ESA_1 and ESA_2 (see next section). These expressions are valid for arbitrary degree of delocalization and therefore, can be further averaged over disorder.

S3. Multiexciton transient absorption (general consideration)

We suppose narrow-band excitation and probe (corresponding to the stationary polarization limit) and restrict to sequential contributions (pump acts the first, probe is the second). The ground-state bleaching (GSB), stimulated emission (SE_1) and the excited-state absorption (ESA_1) corresponding to excitation of one-exciton manifold can be then written in the form [1]:

$$\begin{aligned}
 \text{GSB}(\omega_1, \omega_2) &\propto - \left\langle P_{\text{ex1}} \sum_k d_{\text{kg}}^{e2} d_{\text{gk}}^{e2} \text{Im} \left\{ \frac{\omega_2}{k} \right\} \right\rangle \\
 \text{SE}_1(\omega_1, \omega_2) &\propto - \left\langle P_{\text{ex1}} \sum_k d_{\text{gk}}^{e2} \rho_{\text{kk}} d_{\text{kg}}^{e2} \text{Im} \left\{ \frac{\omega_2}{k} \right\} \right\rangle ; \\
 \text{ESA}_1(\omega_1, \omega_2) &\propto \left\langle P_{\text{ex1}} \sum_{k,q} d_{\text{qk}}^{e2} \rho_{\text{kk}} d_{\text{kq}}^{e2} \text{Im} \left\{ \frac{\omega_2}{qk} \right\} \right\rangle \\
 P_{\text{ex1}} &\propto \sum_{k'} d_{\text{gk}'}^{e1} d_{\text{k}'\text{g}}^{e1} \text{Im} \left\{ L_{\text{k}'\text{g}}^{\omega_1} \right\} ; \\
 L_{\text{k}'\text{g}}^{\omega_1} &= \left((\omega_{\text{k}'} - \omega_1) - iR_{\text{k}'\text{g}} \right)^{-1} \\
 L_{\text{kg}}^{\omega_2} &= \left((\omega_k - \omega_2) - iR_{\text{kg}} \right)^{-1} \\
 F_{\text{kg}}^{\omega_2} &= \left((\omega_k - \lambda_k - \omega_2) - iR_{\text{kg}} \right)^{-1} \\
 L_{\text{qk}}^{\omega_2} &= \left((\omega_{\text{qk}} - \omega_2) - iR_{\text{qk}} \right)^{-1}
 \end{aligned} \tag{S1}$$

where ω_1 and ω_2 are central frequencies of the pump and probe pulses, $\omega_{\text{qk}} = \omega_{\text{q}} - \omega_{\text{k}}$ (where ω_{k} and ω_{q} are defined by eqn (2) and (5) in the main text), λ_{k} is the reorganization energy of the k-th one-exciton state, R_{kg} and R_{qk} denote a homogeneous width of the $|g\rangle \rightarrow |k\rangle$ and $|k\rangle \rightarrow |q\rangle$ transitions, P_{ex1} is the absolute (non-normalized) excitation probability of the complex dependent on its orientation with respect to polarization of the excitation pulse (e1) and excitation frequency ω_1 , d^{e1} and d^{e2} denote a projection of the dipole moment on polarization of the pump (e1) or probe (e2). The angular brackets indicate an averaging over disorder and over orientations of the complex with respect to pump and probe. The SE_1/ESA_1 contributions are dependent on the one-exciton populations ρ_{kk} (normalized). Notice that eqn (S1) do not include one-exciton coherences $\rho_{\text{k}'\text{k}}$ (generalization to coherent case is straightforward). The lineshapes in eqn (S1) correspond to a weak coupling of the electronic transitions to phonons.

The SE_2/ESA_2 contributions corresponding to double-excited aggregate (with populating of the two-exciton states by the pump) are:

$$\begin{aligned}
SE_2(\omega_1, \omega_2) &\propto - \left\langle P_{\text{ex}2} \sum_k d_{kq}^{e2} \rho_{qq} d_{qk}^{e2} \text{Im} \left\{ \frac{\omega_2}{\omega_{qk}} \right\} \right\rangle ; \\
ESA_2(\omega_1, \omega_2) &\propto \left\langle P_{\text{ex}2} \sum_{k,q} d_{rq}^{e2} \rho_{qq} d_{qr}^{e2} \text{Im} \left\{ \frac{\omega_2}{\omega_{rq}} \right\} \right\rangle \\
P_{\text{ex}2} &\propto P_{\text{ex}1} \sum_{q',k''} d_{q'k''}^{e1} \rho_{k''k''} d_{k''q'}^{e1} \text{Im} \left\{ \frac{\omega_1}{\omega_{q'k''}} \right\} ; \\
L_{q'k''}^{\omega_1} &= \left((\omega_{q'k''} - \omega_1) - iR_{q'k''} \right)^{-1} \\
F_{qk}^{\omega_2} &= \left((\omega_{qk} - \lambda_q - \omega_2) - iR_{qk} \right)^{-1} \\
L_{rq}^{\omega_2} &= \left((\omega_{rq} - \omega_2) - iR_{rq} \right)^{-1}
\end{aligned} \tag{S2}$$

where $\omega_{rq} = \omega_r - \omega_q$ (where ω_r is defined by eqn (8) in the main text), λ_q is the reorganization energy of the q -th two-exciton state, R_{rq} is a homogeneous width of the $|q\rangle \rightarrow |r\rangle$ transitions, $P_{\text{ex}2}$ is the absolute (non-normalized) double-excitation probability, ρ_{qq} denote two-exciton populations.

The TA_1 response contains a product of four dipoles projected on polarization of the pump and probe pulses. In this case the orientational averaging rules are [2]:

$$\left\langle (d_{k'g}^{e1})^2 (d_{qk}^{e2})^2 \right\rangle \xrightarrow{\text{m.a.}} \frac{1}{9} \mathbf{d}_{qk}^2 \mathbf{d}_{k'g}^2 \tag{S3}$$

In eqn (S3) the dipoles correspond to ESA_1 (for GSB and SE_1 d_{qk} should be replaced by d_{kg}). We also suppose that the probe is polarized at the magic angle with respect to pump (for other polarizations of the probe the rules are more complicated [2]).

The TA_2 response contains six projections of the transition dipoles [3]. Thus, ESA_2 includes the terms like

$$\left\langle (d_{k'g}^{e1})^2 (d_{q'k''}^{e1})^2 (d_{rq}^{e2})^2 \right\rangle \xrightarrow{\text{m.a.}} \frac{1}{45} \mathbf{d}_{rq}^2 \left[\mathbf{d}_{q'k''}^2 \mathbf{d}_{k'g}^2 + 2(\mathbf{d}_{q'k''} \mathbf{d}_{k'g})^2 \right] \tag{S4}$$

Here we suppose the magic angle between pump and probe polarizations (as in eqn (S3)). For SE_2 d_{rq} should be replaced by d_{qk}

S4. Extraction of multiexciton spectra from experimental data

In this section we show how the TA_1 and TA_2 spectra (used for fitting shown in Fig. 7) have been extracted from the original experimental signal. We use the TA data measured for LH1 antenna complex from the purple bacterium *Rhodobacter sphaeroides* [4]. Here we show the TA spectra corresponding to low and high excitation energies (Fig. S3) and the TA amplitudes measured at 880 and 900 nm as a function of the pump energy (Fig. S4). The TA responses correspond to short-wavelength excitation (840 nm) and zero pump-probe delay (but due to large (up to 10 ps) pulse duration the measured spectra are determined by equilibrated excitations). As shown in Fig. S4 an increase in energy is accompanied by growing of the 900 nm amplitude till saturation at the energies near 10^{16} (photons/cm²). These energies also correspond to saturation of the signal from oxidized reaction center (RC) located within each ring-like LH1 subunit. The RC signal is observed as a bleaching at 810 nm (green points in Fig. S4) at large (500 ps) delay, when the antenna signal disappears due to linear losses and transfers to RC. It means that the energies near 10^{16} correspond to the situation when each LH1 complex absorb one (on average) quantum, so that every RC becomes oxidized after trapping the energy of this quantum. The TA spectral profile measured at this energy (shown by red in Fig. S3) can be therefore assigned to a single-particle TA_1 response. Correspondingly, further increase in excitation energy is expected to cause absorption of more than one quanta accompanied by transformation of the TA profile due to appearance of multi-particle TA components.

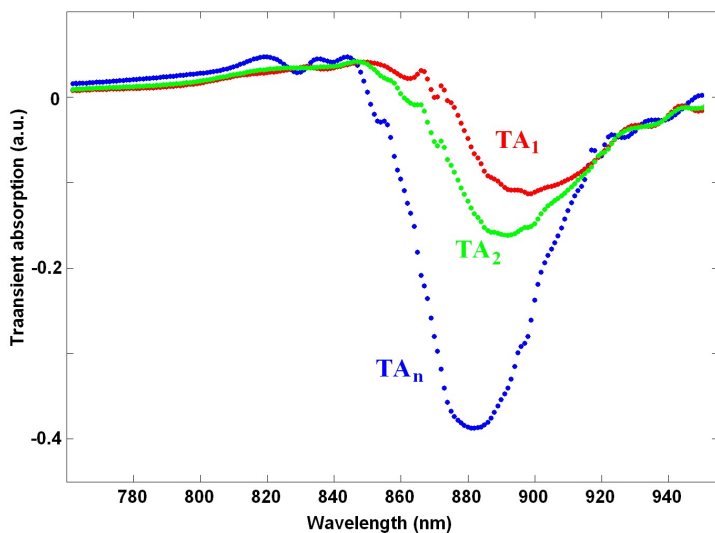


Fig. S3 The TA spectra measured for LH1 antenna complex from the purple bacterium *Rhodobacter sphaeroides* at low (red) and high (blue) excitation energies [4]. The data correspond to short-wavelength excitation (840 nm) and zero pump-probe delay. Due to large (up to 10 ps) pulse duration the measured spectra are determined by equilibrated excitations. The two-particle TA (obtained as linear interpolation between the high- and low-energy profiles) is shown as well (green) (see the text for more detailed explanation).

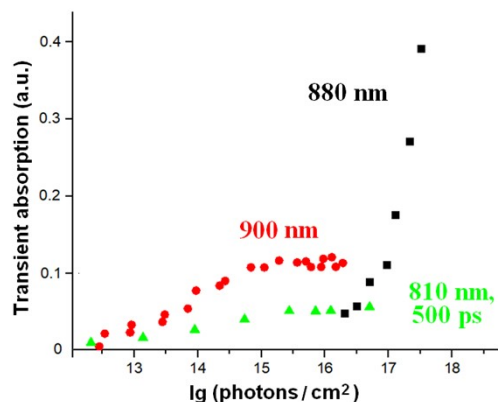


Fig. S4 The TA amplitudes measured at 880 (black) and 900 nm (red) as a function of the pump energy (photons/cm²) (experimental conditions are the same as in Fig. S3). The TA signal from oxidized reaction centers (RC) measured at 810 nm bleaching peak at large (500 ps) delay is shown as well (green).

Measurements of the TA value at higher energies reveal abrupt growing of the 880 nm signal (black points in Fig. S4), thus indicating a blue-shifting of the TA. Due to this shifting the TA profile measured at highest energy (we denote it as TA_n) displays a minimum near 880 nm in contrast with the low-energy TA₁ spectrum with minimum peaking at 896 nm (as shown in Fig. S3). The integrated areas of the TA_n and TA₁ spectra are 5.4:1 (as can be estimated from the data in Fig. S3), meaning that the multi-particle TA_n response corresponds to 5 to 6 (on average) excitations per one LH1 subunit. This ratio is significantly lower than the ratio of the corresponding excitation energies (according to the energy scale in Fig. S4). Therefore, the number of absorbed quanta is more than 5-6 at highest energy, but it is reduced due to annihilation during the pump pulse. Bearing in mind that the timescale of singlet-singlet annihilation in LH1/LH2 complexes [5] is significantly less than our pulse duration, we may suppose that the number of excitations per one complex is in fact determined by a balance between continuous pumping and fast annihilation. The probe pulse is then read-out this quasi-steady-state value, giving 5-6 excitations according to apparent TA area.

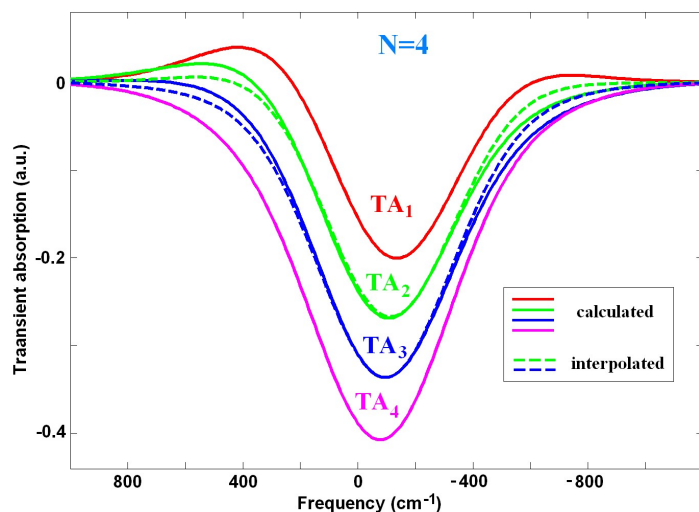


Fig. S5 The multi-particle TA₁-TA₄ spectra (solid lines) calculated for a linear chain made of N=4 molecules with head-to-tail orientations of the transition dipoles). The nearest-neighbour coupling is -50 cm^{-1} , the disorder value is 125 cm^{-1} , homogeneous broadening is modelled by Lorentzian lineshape with the FWHM of 300 cm^{-1} (for ground to one-exciton transitions) and 480 cm^{-1} (for transitions involving multi-exciton manifolds). The TA₂/TA₃ spectra obtained as linear interpolation between the TA₁ and TA₄ profiles are shown as well (dashed lines).

The next step is to extract the two-particle TA_2 spectrum (to use it in our modelling) from the measured TA_n and TA_1 profiles. The simplest way is to use a linear interpolation between the TA_n and TA_1 profiles (corresponding to 5.4 and 1 excitations, respectively) in order to calculate the spectral response expected for a pure two-particle component (corresponding to absorption of exactly 2 excitations), i.e. TA_2 spectrum. The result is shown in Fig. S3. To justify such approach we performed a numerical test for $N=4$ system. The parameters of the system correspond to the same splittings between the exciton levels as in LH1. The ratio of the disorder value and exciton coupling is $\sigma/M=2.5$, that is close to our model of LH1. We calculate multi-particle TA_1 - TA_4 spectra corresponding to 1, 2, 3, and 4 excitations (Fig, S5). Then we calculate the interpolated TA_2/TA_3 spectra (using linear interpolation between the TA_1 and TA_4 profiles). Comparison with the directly calculated TA_2/TA_3 spectra shows that the spectral shifts and amplitudes of the bleaching peaks are reproduced quantitatively well, whereas the tails of the interpolated TA_2/TA_3 profiles display some deviations from the exact shapes. We then conclude that the interpolated two-particle TA_2 spectrum shown in Fig. S3 is reliable, and can be used as a target in our modeling. An example of the fit is shown in Fig. 7 of the main text, where the experimental TA_1 and TA_2 spectra from Fig. S3 are approximated by smooth curves and normalized.

Obviously, the interpolation procedure described above is somehow rough, but useful when the data is restricted to just two TA spectra measured at two different excitation energies (whereas energy-dependent amplitudes are available only at two fixed wavelengths). More accurate and precise definition of the TA_1 , TA_2 , and higher-order components requires more representative sets of the data. Notice in this respect a recently proposed method allowing an isolation of multi-particle contributions from a set of the TA responses measured with N prescribed excitation intensities [6].

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