Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information to
Robust light harvesting by a noisy antenna

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Linear spectra

The expressions for the linear spectra are

$$\begin{aligned} ABS(\omega) &= \omega \sum_k |\mu_{kg}|^2 \mathscr{L}_g(\omega,\omega_k), \\ FL(\omega) &= \omega^3 \sum_k |\mu_{kg}|^2 P_k^{eq} \mathscr{L}_e(\omega,\omega_k). \end{aligned} \tag{1}$$

Here, μ_{kg} are the one-exciton transition dipole moments, $\mu_{kg} = \sum_n c_n^k \mu_n$, and P_k^{eq} is the excited-state quasi-stationary equilibrium population of the $k-th$ excitonic state (calculated by Boltzmann equilibrium, i.e. no nonsecular effects). The $\mathscr{L}_{g/e}$ are the lineshapes arising from the propagation of the optical coherences $\rho_{kg}(t)$ with the bath in the ground/excited state:

$$\mathscr{L}_g(\omega,\omega_k) = \int_0^\infty dt e^{i(\omega-\omega_{kg})t - g_{kkkk}(t) - \frac{\mathscr{R}_{kkkk}}{2}t}, \tag{2}$$

$$\mathscr{L}_e(\omega,\omega_k) = \int_0^\infty dt e^{i(\omega-\omega_{kg}+2i\lambda_{kkkk})t - g^*_{kkkk}(t) - \frac{\mathscr{R}_{kkkk}}{2}t}. \tag{3}$$

Pump-probe spectra

The broadband pump-probe spectra are calculated in the doorway-window picture similar to[? ?]:

$$\begin{aligned} PP_{bb}(\omega,T) &= \sum_{k,n} \mathscr{L}_g(\omega,\omega_k) \langle \mu_{kg},\mu_{kg},\mu_{ng}\mu_{ng}\rangle_{\parallel} + \sum_{k,n} \mathscr{L}_e(\omega,\omega_k) \mathscr{U}_{kk,nn}(T) \langle \mu_{kg},\mu_{kg},\mu_{ng}\mu_{ng}\rangle_{\parallel} \\ &\quad - \sum_f \sum_{k,n} \mathscr{L}_f(\omega,\omega_{fk}) \mathscr{U}_{kk,nn}(T) \langle \mu_{fk},\mu_{fk},\mu_{ng}\mu_{ng}\rangle_{\parallel}. \end{aligned} \tag{4}$$

Here, the contributions are GSB, SE and ESA, respectively, $\langle \bullet \rangle_\Omega$ denotes the orientational average, dependent on the polarization sequence employed. For the broadband pump-probe experiment parallel pulse orientation was used, $\langle a,b,c,d\rangle_{\parallel} = \frac{1}{15}\left((a\cdot b)(c\cdot d) + (a\cdot c)(b\cdot d) + (a\cdot d)(b\cdot c)\right)$. The lineshape for the two-one-exciton coherences is given by

$$\mathscr{L}_f(\omega,\omega_{fk}) = \int_0^\infty dt e^{i(\omega-\omega_{fk}+2(\lambda_{ffkk}-\lambda_{kkkk}))t - g_{kkkk}(t) - g_{ffff}(t) + 2g_{ffkk}(t) - \frac{\Delta_{ffkk}}{2}t}, \tag{5}$$

where

$$\Delta_{ffkk} = \sum_{q\neq f} \sum_{n<m} \sum_{k<l} c_{nm}^f c_{nm}^q c_{kl}^q c_{kl}^f (\delta_{nk}\nu_n + \delta_{nl}\nu_n + \delta_{mk}\nu_m + \delta_{ml}\nu_m) C(\omega_{fq}) + \mathscr{R}_{kkkk} \tag{6}$$

is the 2-exciton lifetime broadening of the 2-1 exciton coherence, without the pure dephasing which is governed by the cumulant expansion. The lineshape functions transform as

$g_{ffkk}(t) = \sum_{n<m}\sum_l \left(c_{nm}^f\right)^2 \left(c_l^k\right)^2 (\delta_{nl}+\delta_{ml})\, g(t)$, $g_{ffff}(t) = \sum_{n<m}\sum_{k<l} \left(c_{nm}^f c_{kl}^f\right)^2 (\delta_{nk}\nu_n + \delta_{nl}\nu_n + \delta_{mk}\nu_m + \delta_{ml}\nu_m)\, g(t)$.The narrowband pump, broadband probe spectrum was calculated as

$$PP_{nb}(\omega,T,\omega_P) = \sum_{k,n}\mathscr{L}_g(\omega,\omega_k)\mathscr{L}_{gp}(\omega_P,\omega_n)\left\langle\mu_{kg},\mu_{kg},\mu_{ng}\mu_{ng}\right\rangle_{m.a.} + \sum_{k,n}\mathscr{L}_e(\omega,\omega_k)\mathscr{U}_{kk,nn}(T)\mathscr{L}_{gp}(\omega_P,\omega_n)\left\langle\mu_{kg},\mu_{kg},\mu_{ng}\mu_{ng}\right\rangle_{m.a.}$$
$$-\sum_f\sum_{k,n}\mathscr{L}_f(\omega,\omega_{fk})\mathscr{U}_{kk,nn}(T)\mathscr{L}_{gp}(\omega_P,\omega_n)\left\langle\mu_{fk},\mu_{fk},\mu_{ng}\mu_{ng}\right\rangle_{m.a.}. \quad (7)$$

Here, the selection of the doorway by the narrowband pump pulse is given by the lineshape including its apparent broadening by interaction with the finite pulse:

$$\mathscr{L}_{gP}(\omega_P,\omega_k) = \int_0^\infty dt e^{i(\omega_P-\omega_{kg})t-g_{kkkk}(t)-\frac{\mathscr{R}_{kkkk}}{2}t-\alpha\frac{t^2}{2}}. \quad (8)$$

This expression is valid for Gaussian pump pulses centered around ω_P and of the envelope $\propto e^{-\alpha t^2}$. This is obtained by integrating the doorway in Eq. A2 of[?] over t' and holds only in strict factorization of the three propagation intervals in the 3rd-order nonlinear response calculation (e.g. no rise of the signal in the waiting time T due to finite pulse duration). The angle between the pump and probe was set to the magic angle 54.7° , yielding the isotropic contribution $\langle a,b,c,d\rangle_{m.a.} = \frac{1}{9}(a\cdot b)(c\cdot d)$. Both the narrow- and broadband calculated pump-probe traces are finally convoluted with a $\sqrt{2}\tau_{pulse}$ wide Gaussian pulse to account for the initial signal decay during the action of the pulse. As we do not calculate the negative-time pathways, we plot only the $T>0$ part.

We note that, including the orientational averaging and averaging over an energetic disorder, the above-described calculation is on the edge of what is achievable on a modern desktop computer.

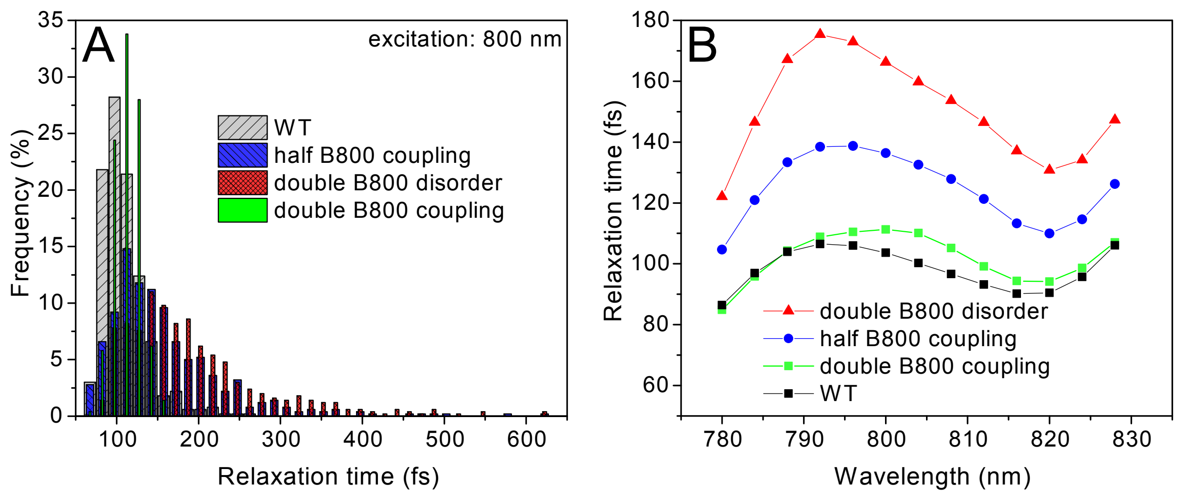

Fig. S 1 Energy relaxation in case of halved (blue) or doubled (green) inter-pigment coupling and doubled B800 ring energy disorder (red). Left: calculated relaxation time distribution excited at 800 nm, right: average relaxation time across the excitonic manifold.

References

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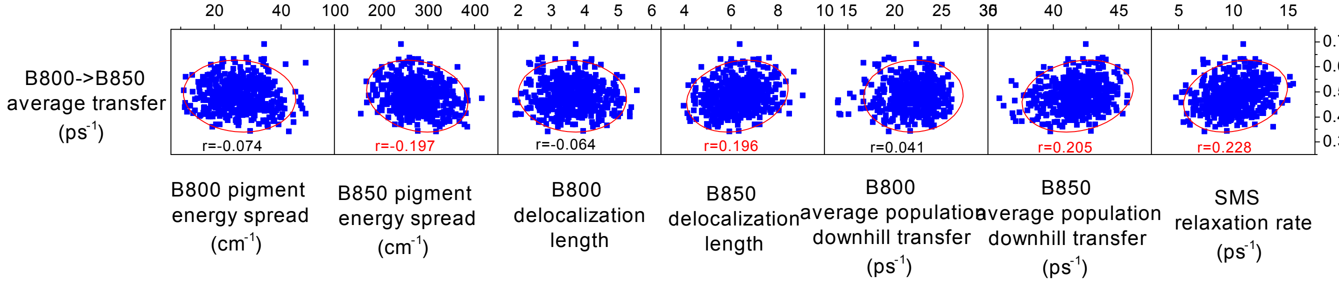
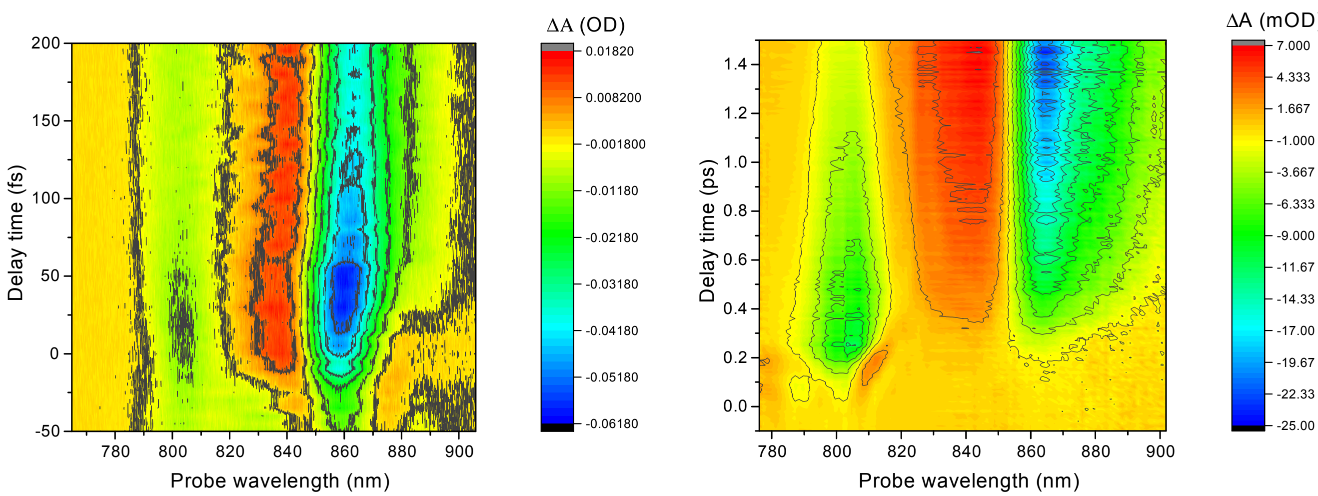


Fig. S2 Correlation of thermally averaged B800->B850 intra-ring energy transfer with the quantities presented in Fig. 5 of the main text. The ellipses are 95% confidence ellipses, the numbers are Pearson's correlation coefficients, red values are $p = 0.05$ significant correlations. The intra-ring transfer is calculated as $\langle k_{800\rightarrow 850}\rangle = \sum_{i\in B800,\, j\in B850} \frac{1}{Z} e^{-\frac{E_i-\lambda_i}{k_BT}} \mathscr{R}_{jj,ii}$, $Z = \sum_{i\in B800} e^{-\frac{E_i-\lambda_i}{k_BT}}$



(a) Broadband TA

(b) Narrowband TA

Fig. S3 Measured broad- and narrowband transient absorption spectra

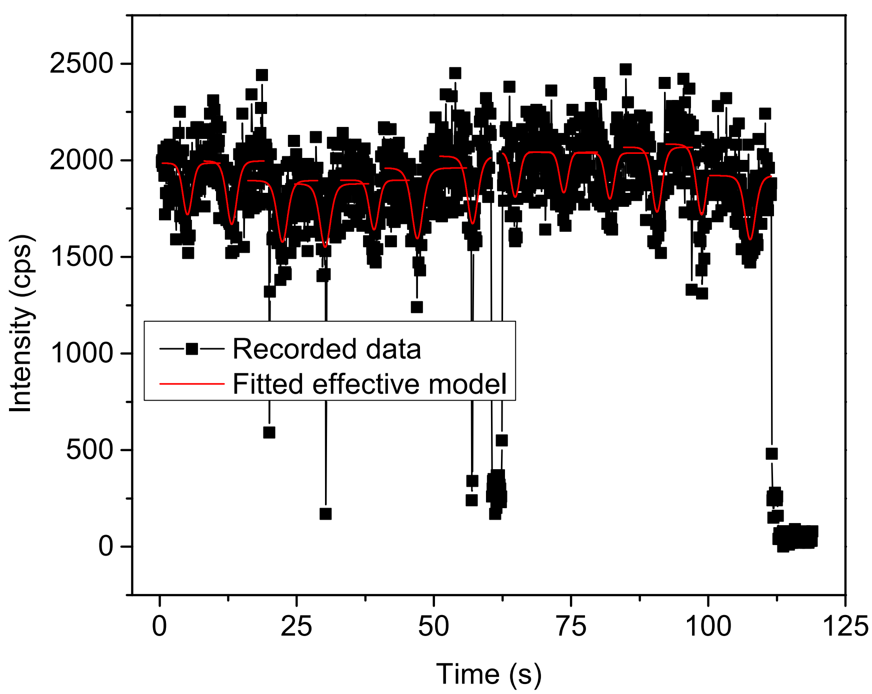


Fig. S4 An exemplary intensity trace of a single LH2 exhibiting blinking behavior and stepwise photobleaching. The dark states are only briefly visited, the LH2 spends most time in the bright state.

12320	355	-48	13	-6	3	-2	1	-1	1	-1	1	-2	2	-6	11	-51	299	-4	-1	-1	-1	-1	-2	-4	25	-11
355	12520	290	-32	11	-4	2	-1	1	0	1	0	1	-1	3	-4	14	-33	6	2	1	1	1	2	5	3	-2
-48	290	12320	372	-51	14	-6	3	-2	1	-1	1	-1	1	-2	2	-6	11	-11	-4	-1	-1	-1	-1	-3	-4	26
13	-32	372	12520	277	-32	11	-4	2	-1	1	0	1	0	1	-1	3	-3	0	6	2	1	1	1	2	5	4
-6	11	-51	277	12320	360	-50	13	-6	3	-2	1	-1	1	-1	1	-2	2	25	-12	-4	-1	-1	-1	-1	-3	-4
3	-4	14	-32	360	12520	311	-34	11	-4	2	-1	1	0	1	0	1	-1	3	0	6	2	1	1	1	2	5
-2	2	-6	11	-50	311	12320	381	-52	14	-6	3	-2	1	-1	1	-1	1	-4	27	-11	-4	-1	-1	-1	-1	-3
1	-1	3	-4	13	-34	381	12520	323	-36	12	-4	2	-1	1	0	1	0	5	3	-4	6	2	1	1	1	2
-1	1	-2	2	-6	11	-52	323	12320	374	-51	14	-6	3	-2	1	-1	1	-3	-4	27	-10	-4	-1	-1	-1	-1
1	0	1	-1	3	-4	14	-36	374	12520	275	-31	11	-4	2	-1	1	0	2	5	3	-2	6	2	1	1	1
-1	1	-1	1	-2	2	-6	12	-51	275	12320	371	-51	14	-6	3	-2	1	-1	-3	-4	26	-10	-4	-1	-1	-1
1	0	1	0	1	-1	3	-4	14	-31	371	12520	285	-33	11	-4	2	-1	1	2	5	4	-1	6	2	1	1
-2	1	-1	1	-1	1	-2	2	-6	11	-51	285	12320	388	-51	14	-6	3	-1	-1	-3	-4	25	-12	-4	-1	-1
2	-1	1	0	1	0	1	-1	3	-4	14	-33	388	12520	276	-33	11	-4	1	1	2	5	3	2	6	2	1
-6	3	-2	1	-1	1	-1	1	-2	2	-6	11	-51	276	12320	383	-53	14	-1	-1	-1	-3	-4	25	-10	-4	-1
11	-4	2	-1	1	0	1	0	1	-1	3	-4	14	-33	383	12520	322	-34	1	1	1	2	5	1	-1	6	2
-51	14	-6	3	-2	1	-1	1	-1	1	-2	2	-6	11	-53	322	12320	360	-1	-1	-1	-1	-3	-3	25	-11	-4
299	-33	11	-3	2	-1	1	0	1	0	1	-1	3	-4	14	-34	360	12520	2	1	1	1	2	5	4	-1	6
-4	6	-11	0	25	3	-4	5	-3	2	-1	1	-1	1	-1	1	-1	2	12520	-23	-3	-1	0	0	-1	-2	-23
-1	2	-4	6	-12	0	27	3	-4	5	-3	2	-1	1	-1	1	-1	1	-23	12520	-23	-3	-1	0	0	-1	-3
-1	1	-1	2	-4	6	-11	-4	27	3	-4	5	-3	2	-1	1	-1	1	-3	-23	12520	-24	-3	-1	0	0	-1
-1	1	-1	1	-1	2	-4	6	-10	-2	26	4	-4	5	-3	2	-1	1	-1	-3	-24	12520	-22	-2	-1	0	0
-1	1	-1	1	-1	1	-1	2	-4	6	-10	-1	25	3	-4	5	-3	2	0	-1	-3	-22	12520	-22	-2	-1	0
-2	2	-1	1	-1	1	-1	1	-1	2	-4	6	-12	2	25	1	-3	5	0	0	-1	-2	-22	12520	-21	-2	-1
-4	5	-3	2	-1	1	-1	1	-1	1	-1	2	-4	6	-10	-1	25	4	-1	0	0	-1	-2	-21	12520	-22	-3
25	3	-4	5	-3	2	-1	1	-1	1	-1	1	-1	2	-4	6	-11	-1	-2	-1	0	0	-1	-2	-22	12520	-22
-11	-2	26	4	-4	5	-3	2	-1	1	-1	1	-1	1	-1	2	-4	6	-23	-3	-1	0	0	-1	-3	-22	12520

Fig. S5 Site Hamiltonian used for the modelling. The B850 ring block is in purple, the B800 block is in red.

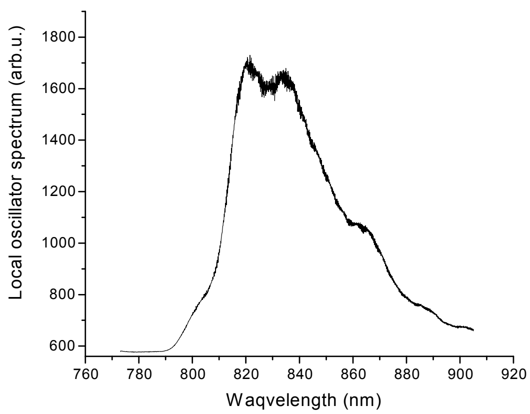
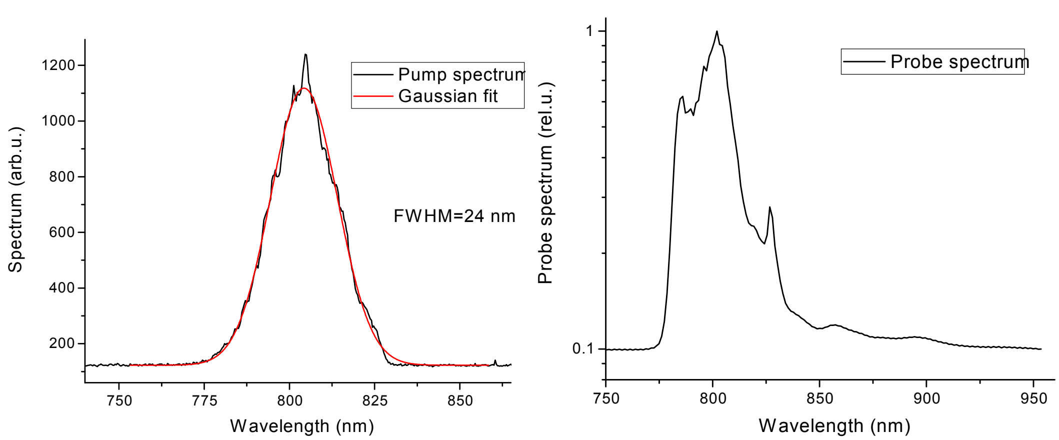


Fig. S6 Pulse spectrum used for the broadband P-P experiment



(a) Pump spectrum

(b) Probe spectrum

Fig. S7 Pulse spectra used for the narrowband P-P experiment