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

Distinguishing the roles of energy funnelling and delocalization in photosynthetic light harvesting

Electronic Supplementary Information

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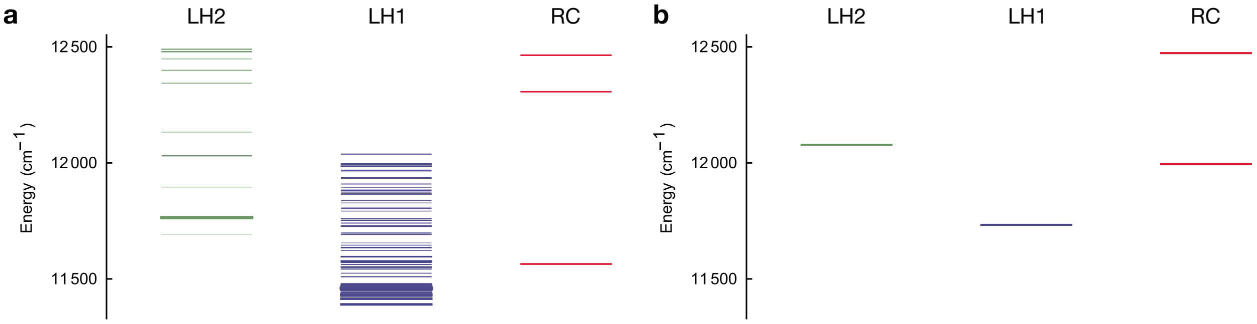


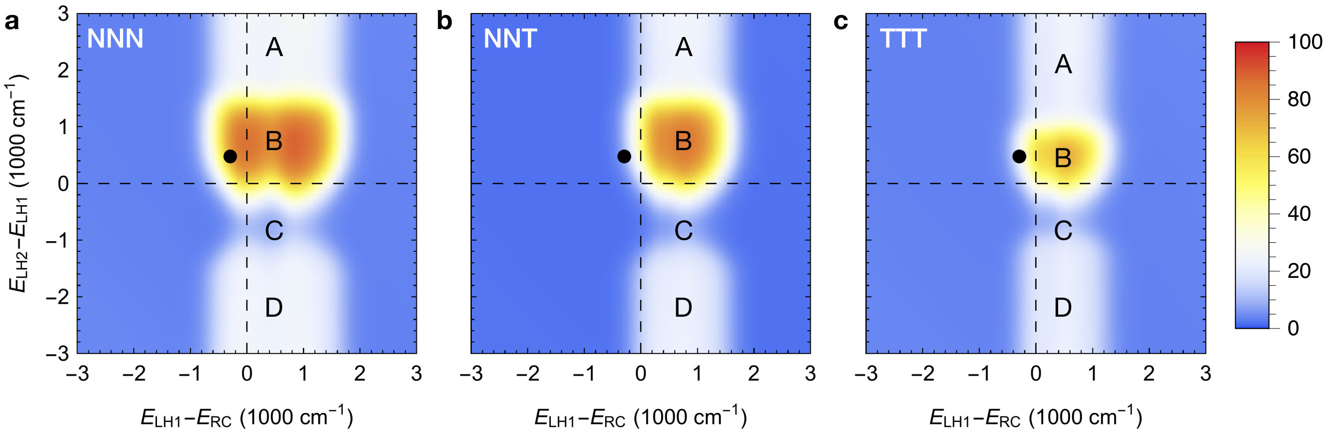
Supplementary Figure 1. Energy levels of the natural **(a)** and trimmed **(b)** complexes in the R parameter set. An important difference with respect to the S-parameter levels shown in Fig. 2 is that LH1 → RC transfer is significantly uphill in the trimmed geometry, explaining the low efficiency of the TTT configuration in the R parameter set.

	Geometry				Transfer times (ps)				
	LH2	LH1	RC	η (%)	LH2 → LH2	LH2 → LH1	LH1 → LH2	LH1 → RC	RC → LH1
S parameters	N	N	N	87	4.5	3.2	35	25	1.9
	N	N	T	12	4.5	3.2	35	3000	19
	N	T	N	53	4.5	16	17	72	55
	N	T	T	39	4.5	16	17	82	5.3
	T	N	N	92	9.6	12	1900	25	1.9
	T	N	T	20	9.6	12	1900	3000	19
	T	T	N	88	9.6	13	200	73	55
	T	T	T	81	9.6	13	200	82	5.3
R parameters	N	N	N	73	17	17	340	156	7.6
	N	N	T	9.3	17	17	340	6400	41
	N	T	N	63	17	26	171	190	27
	N	T	T	15	17	26	172	2200	42
	T	N	N	77	48	43	2400	156	7.6
	T	N	T	12	48	43	2400	6400	42
	T	T	N	73	48	78	1500	190	27
	T	T	T	23	48	78	1500	2200	42

Supplementary Table 1. Efficiencies (η) and inter-complex energy transfer times when the site energies are the original energies listed in Table 1. Our results for the natural geometry NNN in the S parameter set (first line above) are consistent with those of Schulten's group. In particular, our departures from Schulten's approach—treating fewer light-harvesting complexes and using the simplified overlap integral in Eq. 4—are justified because they do not substantially affect the results. Our efficiency and our transfer times for LH1 → RC and RC → LH1 are similar to Schulten's values of, respectively, 78–91% (depending on vesicle structure), 20 ps, and 1.4 ps [1]. Our transfer times involving LH2 are shorter because we assumed a tighter packing based on AFM measurements (compare with Schulten's 10 ps for both LH2 → LH2 and LH2 → LH1 [1]). As noted in the text, this difference largely disappears if the distances are the same. The S parameters tend to agree with experiment somewhat better than the R parameters, although not completely. For example, S parameters get the LH1 → RC transfer time approximately right (estimated at 20 ps at room temperature [2, 3]), but the reverse rate (7–9 ps [4]) is much better captured by the R parameters. Measured transfer times involving LH2 (5 ps for LH2 → LH2 [5] and 3.3 ps for LH2 → LH1 [6]) also agree with those predicted from the S parameters at the separations we used.

	Geometry				Transfer times (ps)				
	LH2	LH1	RC	η (%)	LH2 → LH2	LH2 → LH1	LH1 → LH2	LH1 → RC	RC → LH1
S parameters	N	N	N	98	4.5	4.5	140	4.9	53
	N	N	T	98	4.5	5.2	220	7.4	9.6
	N	T	N	96	4.5	10	390	23	80
	N	T	T	94	4.5	12	640	32	13
	T	N	N	99	9.7	6.4	240	4.9	53
	T	N	T	98	9.7	7.4	410	7.4	9.6
	T	T	N	95	9.7	18	500	23	89
	T	T	T	93	9.7	21	700	32	13
R parameters	N	N	N	89	18	28	1500	70	480
	N	N	T	86	18	32	2100	96	30
	N	T	N	79	20	57	2000	150	1100
	N	T	T	74	17	67	2800	190	37
	T	N	N	89	48	42	2200	70	480
	T	N	T	86	48	45	2600	96	30
	T	T	N	78	48	98	2500	150	1100
	T	T	T	73	48	110	3500	190	37

Supplementary Table 2. Efficiencies (η) and energy transfer times when the site energies are optimised for each geometry.



Supplementary Figure 2. As Fig. 4, but for the R parameter set.

	Geometry				Transfer times (ps)				
	LH2	LH1	RC	η (%)	LH2 → LH2	LH2 → LH1	LH1 → LH2	LH1 → RC	RC → LH1
S params	N	N	T^+	28	4.5	3.2	35	1100	16
	N	T	T^+	58	4.5	16	17	40	6.5
	T	N	T^+	41	9.6	12	1900	1100	16
	T	T	T^+	90	9.6	13	200	40	6.5
R params	N	N	T^+	16	17	17	341	3500	45
	N	T	T^+	24	17	26	172	1200	46
	T	N	T^+	21	48	43	2400	3500	45
	T	T	T^+	35	48	78	1500	1200	46

Supplementary Table 3. Effect of the number of pathways on the efficiency. As noted in the text, having more pathways going away from the RC than towards it implies that entropy drives charges away from the RC. To illustrate this further, we increased the number of BChls in the trimmed RC by replacing the ones that were discarded, indicated as T^+. In other words, we used ordinary FRET on the natural RC geometry, even if that is not the correct description of EET. It can be seen that doubling the number of BChls in each RC roughly doubles the transfer rate LH1 → RC with respect to the values in Supplementary Table 1. This results in an appreciable increase in the efficiency, averaging 75% for the S parameters and 65% for the R parameters (relative to Supplementary Table 1).

Geometry			S parameters		R parameters	
LH2	LH1	RC	η_{Orig} (%)	η_{Opt} (%)	η_{Orig} (%)	η_{Opt} (%)
N	T^3	N	44	95	57	76
N	T^3	T	34	93	12	70
T^3	N	N	92	98	78	90
T^3	N	T	21	98	13	86
T^3	T^3	N	89	95	72	76
T^3	T^3	T	84	93	25	70

Supplementary Table 4. EET efficiencies when the LH2 and/or LH1 aggregates are trimmed more aggressively. T^3 denotes aggregates in which only every third BChl is kept and the results are shown using both the original site energies and the optimal ones. The efficiencies are similar to those obtained with the every-second trimming described in the text, indicating that our conclusions are not sensitive to the extent of trimming.

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