

Supporting Information for:

**Ensemble Study on Energy Transfer from carotenoids to chlorophylls Involving
Two Lutein Pigments in Light-Harvesting Complex II**

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1. Environmental effect.

Table S1: Excitation energy shifts of pigments in a self-consistent convergent charge environment. The results in the three columns are the excitation energies of the pigments in the gas phase, the excitation energies of the pigments in a self-consistent converged charge environment, and the excitation energy shifts of the pigments caused by the environments. (Unit: eV).

	$E_{pigment}^0$	$E_{pigment}^{env}$	$\Delta E_{pigment}^{env}$
$E_{LUT1}^{S_2}$	2.4922	2.3895	-0.1027
$E_{LUT2}^{S_2}$	2.4998	2.3512	-0.1486
$E_{CLA602}^{Q_x}$	2.2768	2.1064	-0.1704
$E_{CLA603}^{Q_x}$	2.2740	2.1449	-0.1291
$E_{CLA604}^{Q_x}$	2.2864	2.2886	0.0022
$E_{CLA610}^{Q_x}$	2.2735	2.2171	-0.0564
$E_{CLA611}^{Q_x}$	2.2799	2.2593	-0.0206
$E_{CLA612}^{Q_x}$	2.2927	2.2783	-0.0144
$E_{CLA613}^{Q_x}$	2.2694	2.2408	-0.0286
$E_{CLA602}^{Q_y}$	2.0822	1.9868	-0.0954
$E_{CLA603}^{Q_y}$	2.0784	1.9547	-0.1237
$E_{CLA604}^{Q_y}$	2.0725	2.0659	-0.0066
$E_{CLA610}^{Q_y}$	2.0712	2.0501	-0.0211
$E_{CLA611}^{Q_y}$	2.0689	2.0499	-0.019

$E_{CLA612}^{Q_y}$	2.0796	2.0864	0.0068
$E_{CLA613}^{Q_y}$	2.0661	2.0551	-0.011

2. Ensemble-averaged result of excitation energies of each pigment.

Table S2: Ensemble average of the excitation energies of the S_2 states of LUTs and the Q_x and Q_y states of CLAs in LHCII environment. (Unit: eV)

	Excitation energy
$E_{LUT1}^{S_2}$	2.359
$E_{LUT2}^{S_2}$	2.356
$E_{CLA602}^{Q_x}$	2.052
$E_{CLA603}^{Q_x}$	2.105
$E_{CLA604}^{Q_x}$	2.246
$E_{CLA610}^{Q_x}$	2.168
$E_{CLA611}^{Q_x}$	2.217
$E_{CLA612}^{Q_x}$	2.223
$E_{CLA613}^{Q_x}$	2.166
$E_{CLA602}^{Q_y}$	1.960
$E_{CLA603}^{Q_y}$	1.916
$E_{CLA604}^{Q_y}$	2.053
$E_{CLA610}^{Q_y}$	2.020
$E_{CLA611}^{Q_y}$	2.026

$E_{CLA612}^{Q_y}$	2.051
$E_{CLA613}^{Q_y}$	1.999

3. Coulomb term ratio in the electronic coupling of each pair of [LUT-CLA].

Table S3-1: The proportion of Coulomb terms in electronic coupling between the S_2 states of LUT1 and the Q_x and Q_y states of CLAs.

Coulombic interaction	
	ratio
$E_{LUT1}^{S_2} - E_{CLA602}^{Q_x}$	0.994
$E_{LUT1}^{S_2} - E_{CLA603}^{Q_x}$	0.993
$E_{LUT1}^{S_2} - E_{CLA604}^{Q_x}$	1.012
$E_{LUT1}^{S_2} - E_{CLA610}^{Q_x}$	1.009
$E_{LUT1}^{S_2} - E_{CLA611}^{Q_x}$	0.997
$E_{LUT1}^{S_2} - E_{CLA612}^{Q_x}$	1.007
$E_{LUT1}^{S_2} - E_{CLA613}^{Q_x}$	1.002
$E_{LUT1}^{S_2} - E_{CLA602}^{Q_y}$	0.992
$E_{LUT1}^{S_2} - E_{CLA603}^{Q_y}$	0.994
$E_{LUT1}^{S_2} - E_{CLA604}^{Q_y}$	1.011
$E_{LUT1}^{S_2} - E_{CLA610}^{Q_y}$	1.021
$E_{LUT1}^{S_2} - E_{CLA611}^{Q_y}$	0.983
$E_{LUT1}^{S_2} - E_{CLA612}^{Q_y}$	1.010

$$E_{LUT1}^{S_2} - E_{CLA613}^{Q_y} \quad 1.012$$

Table S3-2: The proportion of Coulomb terms in electronic coupling between the S_2 states of LUT2 and the Q_x and Q_y states of CLAs.

Coulombic interaction	
	ratio
$E_{LUT2}^{S_2} - E_{CLA602}^{Q_x}$	1.004
$E_{LUT2}^{S_2} - E_{CLA603}^{Q_x}$	1.007
$E_{LUT2}^{S_2} - E_{CLA604}^{Q_x}$	1.009
$E_{LUT2}^{S_2} - E_{CLA610}^{Q_x}$	0.998
$E_{LUT2}^{S_2} - E_{CLA611}^{Q_x}$	0.992
$E_{LUT2}^{S_2} - E_{CLA612}^{Q_x}$	0.993
$E_{LUT2}^{S_2} - E_{CLA613}^{Q_x}$	1.001
$E_{LUT2}^{S_2} - E_{CLA602}^{Q_y}$	0.994
$E_{LUT2}^{S_2} - E_{CLA603}^{Q_y}$	1.016
$E_{LUT2}^{S_2} - E_{CLA604}^{Q_y}$	1.028
$E_{LUT2}^{S_2} - E_{CLA610}^{Q_y}$	0.990
$E_{LUT2}^{S_2} - E_{CLA611}^{Q_y}$	0.994
$E_{LUT2}^{S_2} - E_{CLA612}^{Q_y}$	0.994
$E_{LUT2}^{S_2} - E_{CLA613}^{Q_y}$	1.001

4. Effect of the phase of the wave function.

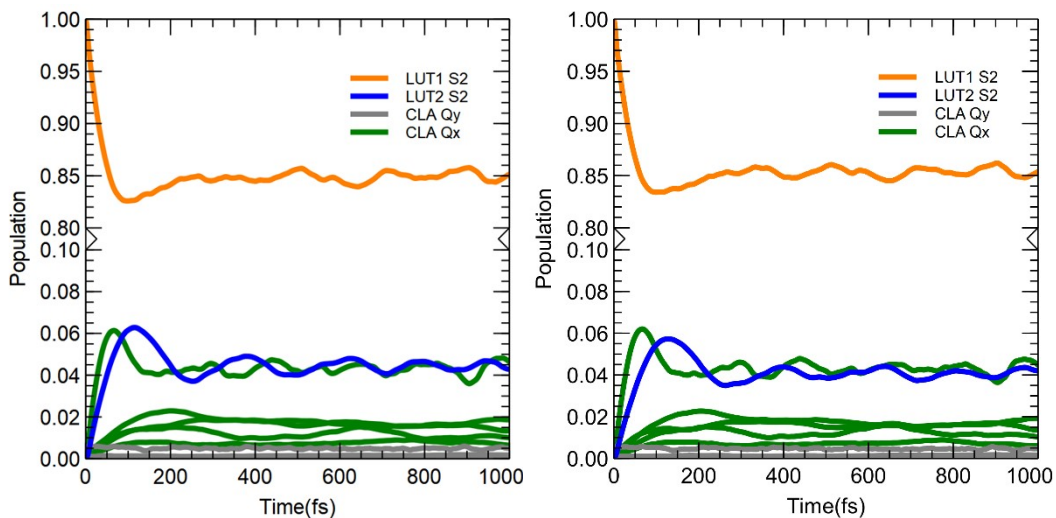


Figure S1: Effect of the phase of the wave function. (a) is the result without considering the phase of the wave function. (b) is the result considering the phase of the wave function.

5. Correction of the wave function phase.

In quantum chemistry calculation, when solving a time-independent Schrödinger equation, the obtained real-valued eigenstate wave function has a random ± 1 phase. When calculating matrix elements between those states (e.g., transition dipole moment), the random phases are carried on to the resultant elements. Hence, in the construction of the Frenkel exciton model, the off-diagonal Hamiltonian matrix elements are affected by the phases.

Here is an example of a system with three chromophores. The local excited states of the three chromophores are labeled as ϕ_i^m , where i indexes a chromophore, and m indexes a state of the chromophore. It is possible for non-diagonal H_{12} to have 16 combinations of the phases.

$$\begin{aligned}
H^{(++++)} &= \int d\vec{r} \phi_1^0 \phi_2^1 \hat{H} \phi_1^1 \phi_2^0, \\
H^{(+++ -)} &= \int d\vec{r} \phi_1^0 \phi_2^1 \hat{H} \phi_1^1 (-\phi_2^0), \\
H^{(++ - +)} &= \int d\vec{r} \phi_1^0 \phi_2^1 \hat{H} (-\phi_1^1) \phi_2^0, \\
H^{(+- + -)} &= \int d\vec{r} \phi_1^0 \phi_2^1 \hat{H} (-\phi_1^1) (-\phi_2^0), \\
H^{(+ - + +)} &= \int d\vec{r} \phi_1^0 (-\phi_2^1) \hat{H} \phi_1^1 \phi_2^0, \\
H^{(+ - - -)} &= \int d\vec{r} \phi_1^0 (-\phi_2^1) \hat{H} \phi_1^1 (-\phi_2^0), \\
H^{(+ - - +)} &= \int d\vec{r} \phi_1^0 (-\phi_2^1) \hat{H} (-\phi_1^1) \phi_2^0, \\
H^{(+ - + -)} &= \int d\vec{r} \phi_1^0 (-\phi_2^1) \hat{H} (-\phi_1^1) (-\phi_2^0), \\
H^{(- + + +)} &= \int d\vec{r} (-\phi_1^0) \phi_2^1 \hat{H} \phi_1^1 \phi_2^0, \\
H^{(- + + -)} &= \int d\vec{r} (-\phi_1^0) \phi_2^1 \hat{H} \phi_1^1 (-\phi_2^0), \\
H^{(- + - +)} &= \int d\vec{r} (-\phi_1^0) \phi_2^1 \hat{H} (-\phi_1^1) \phi_2^0, \\
H^{(- + - -)} &= \int d\vec{r} (-\phi_1^0) \phi_2^1 \hat{H} (-\phi_1^1) (-\phi_2^0), \\
H^{(- - + +)} &= \int d\vec{r} (-\phi_1^0) (-\phi_2^1) \hat{H} \phi_1^1 \phi_2^0, \\
H^{(- - + -)} &= \int d\vec{r} (-\phi_1^0) (-\phi_2^1) \hat{H} \phi_1^1 (-\phi_2^0), \\
H^{(- - - +)} &= \int d\vec{r} (-\phi_1^0) (-\phi_2^1) \hat{H} (-\phi_1^1) \phi_2^0, \\
H^{(- - - -)} &= \int d\vec{r} (-\phi_1^0) (-\phi_2^1) \hat{H} (-\phi_1^1) (-\phi_2^0).
\end{aligned}$$

The 16 combinations are grouped into two sets according to their values, which results in ambiguity:

$$H_{12}^{(+)} = H_{12}^{(++++)} = H_{12}^{(++--)} = H_{12}^{(+-+-)} = H_{12}^{(+--+)} = H_{12}^{(-++-)} = H_{12}^{(-+-+)} = H_{12}^{(----)};$$

$$H_{12}^{(-)} = H_{12}^{(++++)} = H_{12}^{(++--)} = H_{12}^{(+-+-)} = H_{12}^{(+--+)} = H_{12}^{(-++-)} = H_{12}^{(-+-+)} = H_{12}^{(----)};$$

$$H_{12}^{(+)} = -H_{12}^{(-)}$$

Similar ambiguity exists for H_{13} and H_{23} . Adopting $H_{12}^{(+)}$ and $H_{13}^{(-)}$ into the same Hamiltonian matrix may introduce error, e.g., an interchange between constructive interference and destructive interference. Two Hamiltonians with uncertain random phases in their matrix elements lead to incomparable results.

The phases of the Hamiltonian matrix elements can be fixed by examining transition dipole moments. The transition dipole moments between ground and excited states obtained in EET calculation bear the random phases of those states:

$$\mu_{01}^{(+)} = \mu_{01}^{(++)} = \mu_{01}^{(--)};$$

$$\mu_{01}^{(-)} = \mu_{01}^{(+-)} = \mu_{01}^{(-+)};$$

$$\mu_{01}^{(+)} = -\mu_{01}^{(-)}$$

Here, $\mu_{01}^{(+)}$ is the transition dipole between the ground state and the first excited state.

The following correspondence is established between the transition dipole moments and the non-diagonal Hamiltonian matrix elements:

$$(\mu_{01}^{(+)}, \mu_{02}^{(+)}) , (\mu_{01}^{(-)}, \mu_{02}^{(-)}) \mapsto H_{12}^{(+)}$$

$$(\mu_{01}^{(+)}, \mu_{02}^{(-)}) , (\mu_{01}^{(-)}, \mu_{02}^{(+)}) \mapsto H_{12}^{(-)}$$

This correspondence enables us to use the transition dipole moments to ensure consistent phases in the Hamiltonian matrix elements.

We performed principal component analysis (PCA) on transition dipole moments of 1000 samples. Since the distribution of these transition dipole moments will be divided into $\mu^{(+)}$ and $\mu^{(-)}$ clusters in space, the first principal component of which can be

considered as the reference transition dipole direction. For each sample, the directions of the transition dipole moments μ_{01}^{samp} and μ_{02}^{samp} are compared with the references μ_{01}^{ref} and μ_{02}^{ref} :

$$\cos(\mu_{01}^{samp} \wedge \mu_{01}^{ref}), \cos(\mu_{02}^{samp} \wedge \mu_{02}^{ref}).$$

As long as the two cosines have the same sign, the calculated H_{12} is adopted without flipping its sign. Otherwise, the sign of H_{12} is flipped to maintain the same phase as the reference states. Similar phase determinations were performed for all pairs of diabatic states.

6. The energy transfer from two LUTs to each state of CLAs.

Table S4: In the 16-state exciton model, the energy distribution in each state when LUT1 and LUT2 are excited respectively.

	photoexcited	photoexcited
	$S_2(\text{LUT1})$	$S_2(\text{LUT2})$
$E_{LUT1}^{S_2}$	0.85512	0.04070
$E_{LUT2}^{S_2}$	0.04070	0.87307
$E_{CLA602}^{Q_x}$	0.00008	0.00077
$E_{CLA603}^{Q_x}$	0.00049	0.00552
$E_{CLA604}^{Q_x}$	0.00133	0.02935
$E_{CLA610}^{Q_x}$	0.00089	0.00057
$E_{CLA611}^{Q_x}$	0.00099	0.00040
$E_{CLA612}^{Q_x}$	0.00472	0.00209

$E_{CLA613}^{Q_x}$	0.00092	0.00265
$E_{CLA602}^{Q_y}$	0.00032	0.00086
$E_{CLA603}^{Q_y}$	0.00038	0.00247
$E_{CLA604}^{Q_y}$	0.01732	0.01980
$E_{CLA610}^{Q_y}$	0.00681	0.00368
$E_{CLA611}^{Q_y}$	0.01447	0.00162
$E_{CLA612}^{Q_y}$	0.04321	0.00826
$E_{CLA613}^{Q_y}$	0.01225	0.00819

7. The energy transfer pathway with and without LUT2

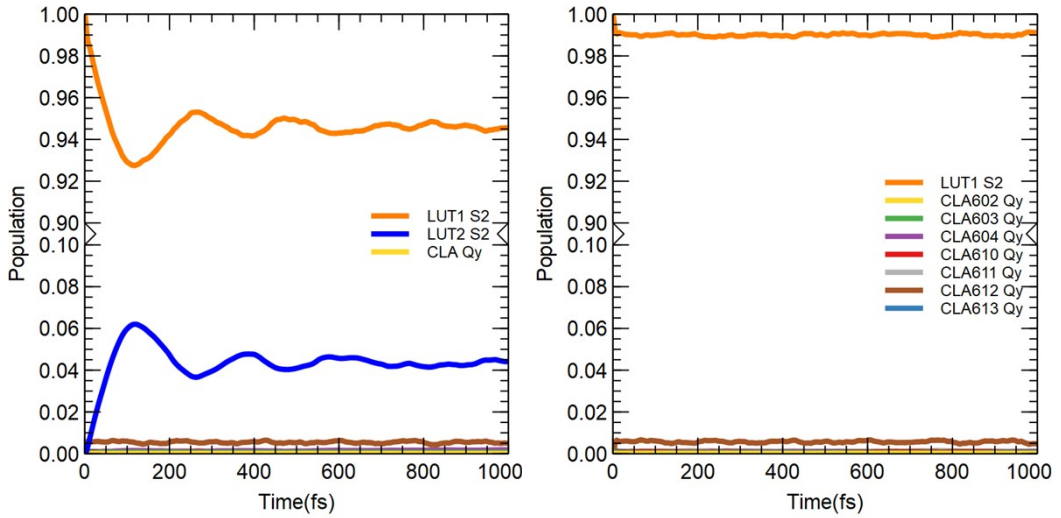


Figure S2: The energy transfer pathway with and without LUT2 S_2 . (a) is the time evolution results of energy transfer from S_2 (LUT1) to Q_y (CLAs) containing S_2 (LUT2), (b) is the time evolution results without S_2 (LUT2).

8. The energy transfer pathway with and without LUT1

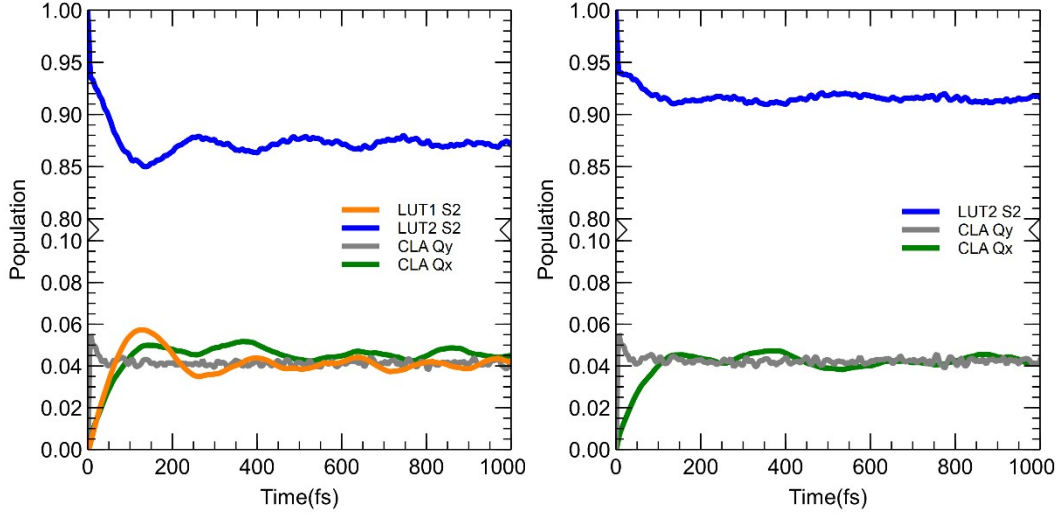


Figure S3: The energy transfer pathway with and without LUT1 S_2 . (a) is the time evolution results of energy transfer from S_2 (LUT2) to Q (CLAs) containing S_2 (LUT1), (b) is the time evolution results without S_2 (LUT1). The green and gray lines are the summations of populations of the seven Q_x and seven Q_y states, respectively.

9. The excitation energies of pigments under different cutoffs.

Table S5: The excitation energies of pigments and the influence of the environment under different cutoffs.

	$E_{pigment}^0$	$E_{pigment}^{env}$ (within 10Å)	$\Delta E_{pigment}^{env}$ (within 10Å)	$E_{pigment}^{env}$ (within 5 Å)	$\Delta E_{pigment}^{env}$ (within 5 Å)
$E_{LUT1}^{S_2}$	2.4922	2.3895	-0.1027	2.4581	-0.0341
$E_{LUT2}^{S_2}$	2.4998	2.3512	-0.1486	2.4198	-0.0800
$E_{CLA602}^{Q_y}$	2.0822	1.9868	-0.0954	1.9737	-0.1085

$E_{CLA603}^{Q_y}$	2.0784	1.9547	-0.1237	1.9305	-0.1479
$E_{CLA604}^{Q_y}$	2.0725	2.0659	-0.0066	2.0572	-0.0153
$E_{CLA610}^{Q_y}$	2.0712	2.0501	-0.0211	2.0723	0.0011
$E_{CLA611}^{Q_y}$	2.0689	2.0499	-0.019	2.0535	-0.0154
$E_{CLA612}^{Q_y}$	2.0796	2.0864	0.0068	2.0798	0.0002
$E_{CLA613}^{Q_y}$	2.0661	2.0551	-0.011	2.0552	-0.0109
$E_{CLA602}^{Q_x}$	2.2768	2.1064	-0.1704	2.0804	-0.1964
$E_{CLA603}^{Q_x}$	2.2740	2.1449	-0.1291	2.0723	-0.2017
$E_{CLA604}^{Q_x}$	2.2864	2.2886	0.0022	2.2701	-0.0163
$E_{CLA610}^{Q_x}$	2.2735	2.2171	-0.0564	2.2864	0.0129
$E_{CLA611}^{Q_x}$	2.2799	2.2593	-0.0206	2.2629	-0.0170
$E_{CLA612}^{Q_x}$	2.2927	2.2783	-0.0144	2.3072	0.0145
$E_{CLA613}^{Q_x}$	2.2694	2.2408	-0.0286	2.2300	-0.0394
