Supporting Information for

Photosynthetic light-harvesting is tuned by the heterogeneous polarizable environment of the protein

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Preparation of the simulation system

The simulated system was based on the X-ray crystal structure of PE545 reported at ultrahigh 0.97 Å resolution (Protein Data Bank ID code 1XG0).[1,2] The missing residues Met-β1, Leu-β2 and Asn-β11 from chain C were carefully added by mimicking the conformation of the equivalent residues in chain D based on an alignment of chain C and D Asp-β3 (for Met-β1 and Leu-β2) or Thr-β10/Ala-β12 (for Asn-β11) residues using the VMD program,[3] where the *i*-Pr group from the resulting Leu-β2 sidechain was rotated by ~150º in order to avoid a steric clash with the close Leu-β27 amino acid. Protonation states of all titratable residues were explored by computing the corresponding pK_as at neutral pH using the automated H++ server (ionic strength 0.15 M, internal and external dielectric constants equal to 15 and 80, respectively).[4-6] All ionizable residues were found to be in the standard ionization state except His-$\alpha_2$16,

which was predicted to be ~50% in its protonated form. However, difference electron density maps[1] suggested that both His-$\alpha_1$16 and His-$\alpha_2$16 are neutral and linked to the protonated form of the DBVs central pyrrole rings *via* a water molecule. Therefore, the standard ionization state was considered also for these residues. All bilin chromophores were modeled having the two central pyrrole rings in their protonated form, again suggested by ultrahigh resolution data.[1] This leads to total -1 charge for each chromophore after consideration of the unprotonated propionate chains. Mg^{2+} and Cl^- ions in the crystal were deleted, as they could arise simply because of the 0.1 M $MgCl_2$ present in the crystallization solution. The system was then neutralized adding two Na^+ ions and solvated in a preequilibrated TIP3P[7] water box (a truncated octahedron with a buffer zone of 12 Å) using the Leap module of the Amber9 suite of programs.[8]

Protein and bilin force field for classical molecular dynamics simulations

The protein and the chromophores were described using the parm99SB[9,10] and the GAFF[11] AMBER force fields, respectively. However, the crystal contained three non-standard residues, two N-methyl asparagines (Men-β72 in chains C and D) and a 5-hydroxylysine (Lyz-$\alpha_1$4). Internal and Van der Waals parameters for these residues were described adopting the corresponding parm99SB atom types, whereas a new set of RESP charges was derived by optimization and subsequent ESP calculations at the HF/6-31G(d) level of Men and Lyz residues capped with N-methyl (NME) and acetyl (ACE) Amber groups. Final RESP charges were then obtained restraining the NME and ACE charges to their Amber values to ensure maximum consistency with the force field as well as an overall integer charge for the residues. Similarly, the charges for the bilin chromophores were obtained at the same level adopting the crystal structures capped with S-methyl groups in the Cys links, where the missing hydrogens were added and

optimized. Then, single sets of charges for the DBV (α19A and α19B), PEB' (β50/61C, β50/61D) and PEB (β158C, β82C, β158D and β82D) chromophores were obtained from multiconformational RESP fittings by restraining the sulfur charge to the Amber CYX residue value and the whole S-methyl charge equal to zero. Quantum chemical calculations were performed using the Gaussian 09 package.[12]

Calculation of the optical dielectric constant from atomic polarizabilities

The calculation of the optical dielectric constant directly from the set of atomic polarizabilities have been performed first by internal contraction of the relay matrix, i.e. the matrix connecting the induced dipoles and the external field, providing the molecular polarizability of the system under investigation[13] and next by application of the equation

$$\varepsilon_{opt} = 1 + \frac{4\pi\alpha}{V} \qquad [1]$$

where α is the calculated molecular polarizability and *V* is the volume of the system estimated by constructing a van der Waals surface from unscaled Bondi atomic radii as implemented in the SCRF keyword in Gaussian09.[12]

Dissection of MMPol environment-mediated coupling contributions

The MMPol method relies on a mixed quantum mechanics/molecular mechanics (QM/MM) scheme, where the chromophores are described at the quantum mechanical level whereas the protein—solvent enviroment is described through a classical polarizable force field. Within this framework, the effective Hamiltonian includes the contributions from the MM residual charges, as well as a mutual account of chromophore—environment polarization.[14,15] The electronic coupling, to first-order, writes:

$$V = V_s + V_{explicit} \quad [2]$$

where V_s describes the interaction between donor—acceptor transition densities

$$V_s = \int d\mathbf{r} \int d\mathbf{r}' \rho_A^{T*}(\mathbf{r}') \left(\frac{1}{|\mathbf{r}' - \mathbf{r}|} + g_{xc}(\mathbf{r}', \mathbf{r}) \right) \rho_D^T(\mathbf{r}) - \omega_0 \int d\mathbf{r} \rho_A^{T*}(\mathbf{r}) \rho_D^T(\mathbf{r}) \quad [3]$$

and $V_{explicit}$ describes the explicit environment-mediated contribution to the electronic coupling

$$V_{explicit} = -\sum_k \left(\int d\mathbf{r} \rho_A^{T*}(\mathbf{r}) \frac{(\mathbf{r}_k - \mathbf{r})}{|\mathbf{r}_k - \mathbf{r}|^3} \right) \mu_k^{ind}(\rho_D^T) \quad [4]$$

where ρ_D^T and ρ_A^T indicate transition densities calculated for the solvated donor and acceptor chromophores, respectively, in the absence of their interaction, g_{xc} is the exchange eventually plus correlation (if a density functional theory description is used) kernel, ω_0 indicates the resonant transition energy and r is the electronic coordinate.

In eq 4 the index k runs over the total number of induced dipoles μ_k^{ind}, located at r_k, associated to each polarizable MM sites. From that expression, it is straightforward to dissect the $V_{explicit}$ term into contributions associated to structural groups of the system:

$$V_{explicit} = \sum_N V_{explicit}^N = -\sum_N \sum_{k \in N} \left(\int d\mathbf{r} \rho_A^{T*}(\mathbf{r}) \frac{(\mathbf{r}_k - \mathbf{r})}{|\mathbf{r}_k - \mathbf{r}|^3} \right) \mu_k^{ind}(\rho_D^T) \quad [4]$$

where each MM site k is assigned a group N in the system.

Computational details of MMPol electronic coupling calculations

All MMPol calculations were performed at the configuration interaction with singles (CIS) level of theory using the 6-31G basis set. For each structure, MMPol calculations are obtained for three model systems accounting only for the protein, the protein plus biological water, and the full protein-water system. Biological or bound waters within 3 Å of the protein or bilin atoms were considered. Induced dipoles in the MM region were

iterated until the root mean square deviation between the dipoles obtained between succesive iterations dropped below 10^{-5} a.u. In PE545 all chromophores are covalently bonded to a Cys residue. In order to separate the protein from the chromophores we cut through the Cα-Cβ bond and saturated with hydrogen atoms both the chromophores and the backbone. This effectively changes the affected Cys's into Gly's. In the MMPol calculations, all charges and polarizabilities were set equal to zero for MM sites in close contact (i.e. within 1.4 Å) to a QM atom, i.e. the Cα and Hα atoms of the Cys's where chromophores are covalently bonded. In all QM/MM calculations all charges in the system were fully considered, whereas polarizabilities from atoms placed further than 18 Å from any QM atom where neglected.

References

Complete references 20 and 27 in the main article are provided as references 8 and 12, respectively.

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Table S1. Effective dielectric permittivities and corresponding standard deviations obtained from MMPol calculations including the protein, protein+bound water, or the complete protein-water system. Results are averaged over 141 snapshots extracted from a molecular dynamics simulation of the PE545 complex. In addition, permittivities obtained by describing the protein-water environment as a continuum dielectric and adopting the arrangement of the chromophores as found in the crystal structure are also shown.

	MMPol						Continuum dielectric
	Protein		Protein+bound water		Protein+bound and bulk water		Protein+bound and bulk water
Molecule pair	$<\varepsilon_{eff}>$	σ	$<\varepsilon_{eff}>$	σ	$<\varepsilon_{eff}>$	σ	ε_{eff}
DBV_{19A} — DBV_{19B}	0.92	0.04	1.13	0.04	1.35	0.03	1.72
DBV_{19A} — $PEB_{50/61C}$	--	--	--	--	--	--	--
DBV_{19A} — PEB_{158C}	1.66	0.09	2.17	0.14	2.25	0.12	1.86
DBV_{19A} — PEB_{82C}	1.27	0.04	1.39	0.04	1.60	0.04	1.85
DBV_{19A} — $PEB_{50/61D}$	1.41	0.04	1.57	0.05	1.78	0.05	1.85
DBV_{19A} — PEB_{158D}	1.58	0.07	1.61	0.05	1.68	0.05	1.93
DBV_{19A} — PEB_{82D}	1.37	0.05	1.60	0.06	1.82	0.06	1.76
DBV_{19B} — $PEB_{50/61C}$	1.48	0.05	1.63	0.05	1.83	0.05	1.86
DBV_{19B} — PEB_{158C}	1.39	0.06	1.49	0.05	1.62	0.05	1.92
DBV_{19B} — PEB_{82C}	1.36	0.05	1.58	0.06	1.78	0.06	1.76
DBV_{19B} — $PEB_{50/61D}$	--	--	--	--	--	--	--
DBV_{19B} — PEB_{158D}	1.46	0.11	1.99	0.17	2.12	0.15	1.87
DBV_{19B} — PEB_{82D}	1.29	0.03	1.39	0.03	1.61	0.03	1.85
$PEB_{50/61C}$ — PEB_{158C}	1.55	0.05	1.86	0.07	2.20	0.07	1.81
$PEB_{50/61C}$ — PEB_{82C}	1.66	0.05	1.82	0.07	1.99	0.07	1.85
$PEB_{50/61C}$ — $PEB_{50/61D}$	2.20	0.14	2.62	0.18	2.57	0.15	1.77

$PEB_{50/61C}$ — PEB_{158D}	1.96	0.22	1.82	0.12	1.90	0.10	2.20
$PEB_{50/61C}$ — PEB_{82D}	1.62	0.06	1.73	0.07	1.85	0.06	1.92
PEB_{158C} — PEB_{82C}	1.34	0.04	1.46	0.04	1.59	0.05	1.91
PEB_{158C} — $PEB_{50/61D}$	1.52	0.15	1.62	0.14	1.71	0.10	2.04
PEB_{158C} — PEB_{158D}	1.35	0.06	1.54	0.05	1.70	0.05	1.80
PEB_{158C} — PEB_{82D}	1.20	0.05	1.35	0.06	1.58	0.06	1.87
PEB_{82C} — $PEB_{50/61D}$	1.60	0.05	1.74	0.05	1.86	0.05	1.91
PEB_{82C} — PEB_{158D}	1.38	0.06	1.46	0.06	1.66	0.06	1.89
PEB_{82C} — PEB_{82D}	1.08	0.06	1.08	0.06	1.36	0.05	1.83
$PEB_{50/61D}$ — PEB_{158D}	1.66	0.05	2.01	0.07	2.43	0.11	1.77
$PEB_{50/61D}$ — PEB_{82D}	1.46	0.03	1.68	0.04	1.88	0.04	1.83
PEB_{158D} — PEB_{82D}	1.34	0.04	1.45	0.04	1.58	0.04	1.90
Mean	1.47	0.07	1.65	0.07	1.82	0.07	1.89

Table S2. Dissection of the MMPol environment-mediated term to the electronic coupling into contributions induced by different structural groups of the PE545-water system (chain A, chain B, chain C, chain D, waters, and bilin chromophores different than the actual interacting molecular pair). In particular, results indicate the percent changes in the coupling induced by each group with respect to the chromophore-chromophore direct coupling term, i.e. $\%Group = \left(V_{explicit}^{Group} / V_s\right) \times 100$, and are averaged over 141 snapshots extracted from a molecular dynamics simulation of the complex. Negative and positive terms contribute either a screening or an enhancement of the interaction between sites, respectively.

Molecule pair	Chain A	Chain B	Chain C	Chain D	Bilins	Waters
DBV_{19A} — DBV_{19B}	-17	-18	22	25	1	-38
DBV_{19A} — $PEB_{50/61C}$	-53	10	-17	16	22	-7
DBV_{19A} — PEB_{158C}	-15	-15	-18	12	1	-20
DBV_{19A} — PEB_{82C}	8	-10	-24	7	1	-20
DBV_{19A} — $PEB_{50/61D}$	-8	-16	3	-4	1	-20
DBV_{19A} — PEB_{158D}	-17	1	-4	-15	0	-6
DBV_{19A} — PEB_{82D}	-2	-14	2	-6	-1	-24
DBV_{19B} — $PEB_{50/61C}$	-21	-8	-1	2	1	-18
DBV_{19B} — PEB_{158C}	1	-10	-13	-4	0	-12
DBV_{19B} — PEB_{82C}	-13	-1	-6	2	-1	-24
DBV_{19B} — $PEB_{50/61D}$	-24	48	-87	32	-50	26
DBV_{19B} — PEB_{158D}	-11	-18	15	-17	2	-24
DBV_{19B} — PEB_{82D}	-11	8	7	-25	1	-18
$PEB_{50/61C}$ — PEB_{158C}	-4	-1	-16	-4	-3	-25
$PEB_{50/61C}$ — PEB_{82C}	-12	-1	-20	-3	0	-14
$PEB_{50/61C}$ — $PEB_{50/61D}$	-12	1	-25	-13	0	-11

$PEB_{50/61C}$ — PEB_{158D}	2	4	-11	-39	0	-4
$PEB_{50/61C}$ — PEB_{82D}	-8	7	-11	-28	4	-11
PEB_{158C} — PEB_{82C}	12	-4	-33	-1	2	-14
PEB_{158C} — $PEB_{50/61D}$	8	9	-37	-18	4	-7
PEB_{158C} — PEB_{158D}	0	2	-13	-10	-2	-18
PEB_{158C} — PEB_{82D}	21	13	-40	-10	1	-21
PEB_{82C} — $PEB_{50/61D}$	9	0	-30	-15	2	-12
PEB_{82C} — PEB_{158D}	0	17	-8	-34	2	-17
PEB_{82C} — PEB_{82D}	13	22	-13	-23	-1	-24
$PEB_{50/61D}$ — PEB_{158D}	-1	4	-7	-25	-4	-26
$PEB_{50/61D}$ — PEB_{82D}	2	-1	-4	-21	0	-22
PEB_{158D} — PEB_{82D}	-5	12	-1	-32	3	-13

Table S3. Total electronic couplings (in cm^{-1}) and corresponding standard deviations obtained from MMPol calculations including the protein, protein+bound water, or the complete protein-water system. Results are averaged over 141 snapshots extracted from a molecular dynamics simulation of the PE545 complex. In addition, electronic couplings obtained by describing the protein-water environment as a continuum dielectric and adopting the arrangement of the chromophores as found in the crystal structure are also shown.

	MMPol						Continuum dielectric
	Protein		Protein+bound water		Protein+bound and bulk water		Protein+bound and bulk water
Molecule pair	$\langle V \rangle$	σ	$\langle V \rangle$	σ	$\langle V \rangle$	σ	V
DBV_{19A} — DBV_{19B}	-6	1	-5	0	-4	0	-4
DBV_{19A} — $PEB_{50/61C}$	2	1	2	1	2	1	2
DBV_{19A} — PEB_{158C}	-36	5	-28	4	-27	4	-32
DBV_{19A} — PEB_{82C}	-14	1	-13	1	-11	1	-11
DBV_{19A} — $PEB_{50/61D}$	-47	4	-44	3	-39	3	-37
DBV_{19A} — PEB_{158D}	4	0	4	0	3	0	3
DBV_{19A} — PEB_{82D}	44	5	39	4	34	4	46
DBV_{19B} — $PEB_{50/61C}$	-51	4	-48	4	-43	4	-35
DBV_{19B} — PEB_{158C}	-4	0	-4	0	-4	0	-3
DBV_{19B} — PEB_{82C}	-46	6	-41	5	-36	5	-45
DBV_{19B} — $PEB_{50/61D}$	2	2	2	1	1	1	3
DBV_{19B} — PEB_{158D}	35	6	28	6	26	5	31
DBV_{19B} — PEB_{82D}	14	1	13	1	12	1	11
$PEB_{50/61C}$ — PEB_{158C}	-30	3	-25	3	-22	3	-20
$PEB_{50/61C}$ — PEB_{82C}	40	3	37	3	34	3	36
$PEB_{50/61C}$ — $PEB_{50/61D}$	77	15	69	13	72	13	107

$PEB_{50/61C}$ — PEB_{158D}	23	5	25	4	24	4	12
$PEB_{50/61C}$ — PEB_{82D}	13	1	13	1	12	1	16
PEB_{158C} — PEB_{82C}	9	1	8	1	7	1	7
PEB_{158C} — $PEB_{50/61D}$	-17	4	-16	4	-15	3	-16
PEB_{158C} — PEB_{158D}	-7	1	-7	1	-6	1	-6
PEB_{158C} — PEB_{82D}	8	1	7	1	6	1	7
PEB_{82C} — $PEB_{50/61D}$	-18	1	-17	1	-16	1	-18
PEB_{82C} — PEB_{158D}	8	1	7	1	7	1	5
PEB_{82C} — PEB_{82D}	5	1	5	1	4	1	3
$PEB_{50/61D}$ — PEB_{158D}	27	3	23	3	19	3	25
$PEB_{50/61D}$ — PEB_{82D}	-44	3	-40	3	-36	3	-39
PEB_{158D} — PEB_{82D}	9	1	9	1	8	1	7

Table S4. Distances, orientation factors, and unscreened dipole-dipole couplings calculated for the complete PE545-water system from transition dipoles extracted from MMPol calculations. Results are averaged over 141 snapshots extracted from a molecular dynamics simulation of the complex.

Molecule pair	$\langle R \rangle$ / Å	σ	$\langle \kappa \rangle$	σ	$\langle V_{dip\text{-}dip} \rangle$ / cm^{-1}	σ
DBV_{19A} — DBV_{19B}	44.8	0.5	-0.697	0.063	-7	1
DBV_{19A} — $PEB_{50/61C}$	32.3	0.4	0.186	0.090	4	2
DBV_{19A} — PEB_{158C}	20.6	0.4	-0.341	0.074	-32	8
DBV_{19A} — PEB_{82C}	34.5	0.4	-1.021	0.047	-21	2
DBV_{19A} — $PEB_{50/61D}$	23.4	0.3	-1.135	0.046	-72	5
DBV_{19A} — PEB_{158D}	46.8	0.4	0.703	0.059	6	1
DBV_{19A} — PEB_{82D}	24.1	0.4	1.174	0.109	70	6
DBV_{19B} — $PEB_{50/61C}$	23.5	0.4	-1.261	0.043	-75	5
DBV_{19B} — PEB_{158C}	47.3	0.5	-0.767	0.056	-6	0
DBV_{19B} — PEB_{82C}	24.0	0.4	-1.163	0.088	-71	7
DBV_{19B} — $PEB_{50/61D}$	30.9	0.3	0.104	0.076	3	2
DBV_{19B} — PEB_{158D}	20.3	0.3	0.236	0.082	24	9
DBV_{19B} — PEB_{82D}	34.4	0.4	1.018	0.040	21	1
$PEB_{50/61C}$ — PEB_{158C}	26.1	0.3	-1.171	0.093	-44	5
$PEB_{50/61C}$ — PEB_{82C}	23.4	0.3	1.018	0.056	55	4
$PEB_{50/61C}$ — $PEB_{50/61D}$	17.2	0.3	0.930	0.103	123	15
$PEB_{50/61C}$ — PEB_{158D}	22.0	0.4	0.529	0.067	34	5
$PEB_{50/61C}$ — PEB_{82D}	34.5	0.3	1.121	0.037	19	1
PEB_{158C} — PEB_{82C}	37.2	0.3	0.689	0.053	10	1
PEB_{158C} — $PEB_{50/61D}$	23.2	0.5	-0.331	0.080	-19	5
PEB_{158C} — PEB_{158D}	44.4	0.5	-1.064	0.078	-9	1
PEB_{158C} — PEB_{82D}	38.9	0.4	0.735	0.088	9	1

PEB_{82C} — $PEB_{50/61D}$	33.2	0.3	-1.207	0.031	-24	1
PEB_{82C} — PEB_{158D}	38.1	0.3	0.736	0.083	10	1
PEB_{82C} — PEB_{82D}	36.8	0.4	0.365	0.048	6	1
$PEB_{50/61D}$ — PEB_{158D}	25.0	0.3	0.975	0.086	46	4
$PEB_{50/61D}$ — PEB_{82D}	22.8	0.2	-0.870	0.052	-53	4
PEB_{158D} — PEB_{82D}	37.2	0.3	0.739	0.044	11	1

Table S5. Average transition dipoles (in Debye) and corresponding standard deviations obtained from MMPol calculations including the protein, protein+bound water, or the complete protein-water system. Results are averaged over 141 snapshots extracted from a molecular dynamics simulation of the PE545 complex. In addition, transition dipoles obtained by describing the protein-water environment as a continuum dielectric and adopting the arrangement of the chromophores as found in the crystal structure are also shown.

	MMPol						Continuum dielectric
	Protein		Protein+bound water		Protein+bound and bulk water		Protein+bound and bulk water
Molecule	$<\mu^T>$	σ	$<\mu^T>$	σ	$<\mu^T>$	σ	μ^T
DBV_{19A}	13.3	0.3	13.5	0.4	13.5	0.4	12.9
DBV_{19B}	13.5	0.4	13.7	0.4	13.7	0.4	12.9
$PEB_{50/61C}$	11.1	0.3	11.2	0.3	11.2	0.3	12.0
PEB_{158C}	11.7	0.3	11.8	0.4	11.8	0.4	11.9
PEB_{82C}	12.1	0.3	12.2	0.3	12.2	0.3	12.3
$PEB_{50/61D}$	11.4	0.4	11.8	0.3	11.9	0.3	11.7
PEB_{158D}	12.0	0.3	12.1	0.3	12.2	0.3	12.1
PEB_{82D}	12.1	0.3	12.2	0.3	12.2	0.3	12.4

Table S6. Energy transfer times (in ps) between delocalized eigenstates of the PE545 complex computed either from MMPol electronic couplings obtained for the full PE545-water system or from continuum dielectric calculations. MMPol results are averaged over 141 snapshots extracted from a molecular dynamics simulation of the PE545 complex, whereas continuum dielectric results are obtained from the arrangement of the chromophores as found in the crystal structure.

MMPol								
	DBV_{19A}	DBV_{19B}	PEB_{158C}	PEB_{158D}	$PEB_{50/61C}$	$PEB_{50/61D}$	PEB_{82C}	PEB_{82D}
DBV_{19A}	--	5	977	9019	61	2733	7	1111
DBV_{19B}	2	--	353	252	50	13956	1	680
PEB_{158C}	71	72	--	698	127	1528	24	5715
PEB_{158D}	186	14	199	--	71	247	42	972
$PEB_{50/61C}$	8	17	239	467	--	337	9	4228
$PEB_{50/61D}$	3	39	25	14	3	--	26	41
PEB_{82C}	2	1	82	528	16	5841	--	582
PEB_{82D}	14	24	1055	622	412	466	31	--
Continuum dielectric								
	DBV_{19A}	DBV_{19B}	PEB_{158C}	PEB_{158D}	$PEB_{50/61C}$	$PEB_{50/61D}$	PEB_{82C}	PEB_{82D}
DBV_{19A}	--	10	562	8661	126	4135	12	648
DBV_{19B}	2	--	361	187	20	7650	1	458
PEB_{158C}	31	107	--	2328	161	1039	32	10227
PEB_{158D}	142	16	682	--	181	240	31	1768
$PEB_{50/61C}$	13	11	300	1151	--	134	11	1884
$PEB_{50/61D}$	3	32	14	11	1	--	8	39
PEB_{82C}	2	0	71	238	13	1353	--	311
PEB_{82D}	6	24	1808	1067	178	489	25	--