Supporting Information for "Exciton Delocalization and Energy Transport Mechanisms in R-Phycoerythrin"

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I. Calculations of Transition Dipoles

Below we describe the procedure used to generate transition dipole orientations for the five unique pigments in R-Phycoerythrin. All calculations utilize Gaussian 2003 and Gaussview version 3.09. TDDFT calculations were performed at the B3LYP/6-31G level, where each pigment possessed a neutral charge and singlet spin multiplicity. The Integral Equation Formalism Polarizable Continuum Model (IEF-PCM) was employed, with the dielectric constant set equal to 4, to mimic the environment inside the protein.[1] Variation of the dielectric constant between 1 and 80 produced negligible changes in the orientations of the transition dipoles. All transition dipoles orientations are depicted below in Figures S1 – S5. Atomic coordinates were obtained from the 1B8D PDB file.

II. Transient Absorption Anisotropies

Figure S6 shows the absorptive parts of the individual tensor elements, $S_{ZZZZ}(T)$ (black) and $S_{ZZXX}(T)$ (red), used to generate the anisotropies shown in Figure 7 of the main paper.

Figure S1

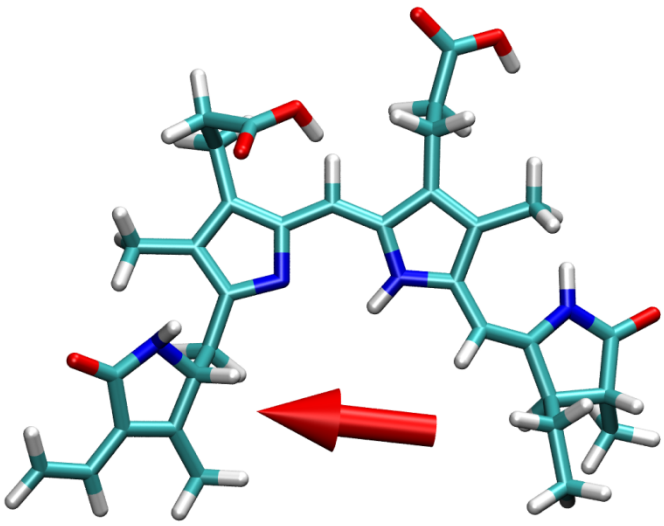

Figure S1. Structure of phycoerythrobilin bonded to residue β82 overlaid with its calculated transition dipole (red arrow). The transition dipole was found as described in Section I using the above structure as input in TDDFT calculations. This image was generated using Visual Molecular Dynamics.[2]

Figure S2

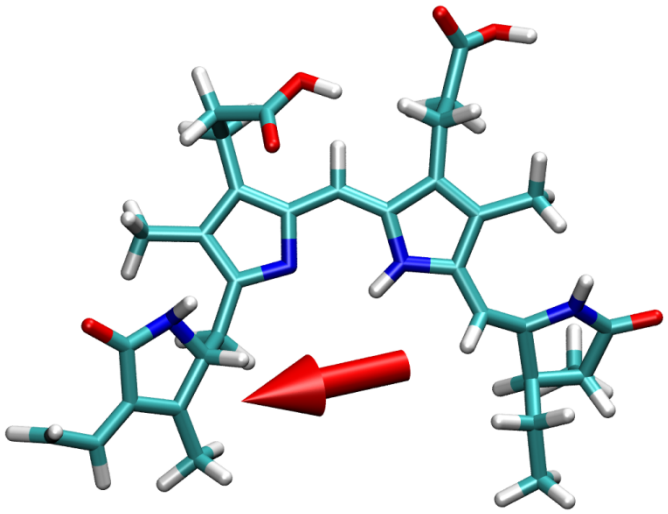

Figure S2. Structure of phycoerythrobilin bonded to residue α82 overlaid with its calculated transition dipole (red arrow). The transition dipole was found as described in Section I using the above structure as input in TDDFT calculations. This image was generated using Visual Molecular Dynamics.[2]

Figure S3

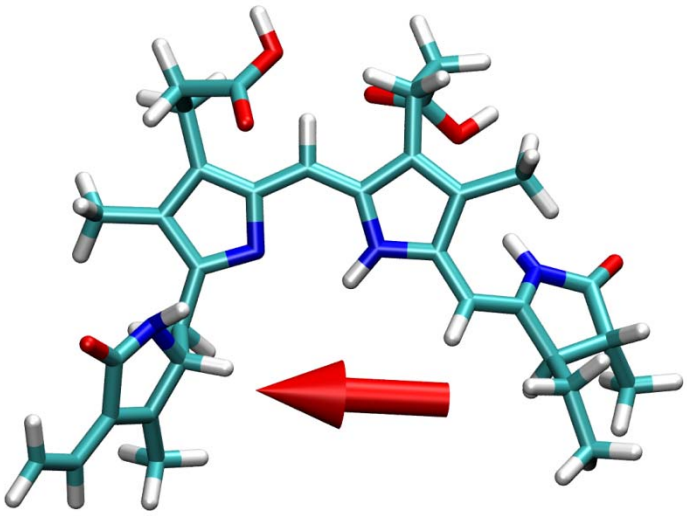

Figure S3. Structure of phycoerythrobilin bonded to residue α139 overlaid with its calculated transition dipole (red arrow). The transition dipole was found as described in Section I using the above structure as input in TDDFT calculations. This image was generated using Visual Molecular Dynamics.[2]

Figure S4

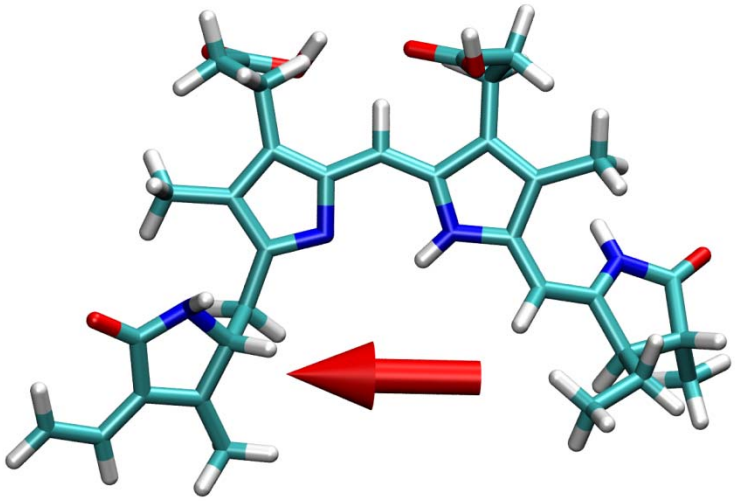

Figure S4. Structure of phycoerythrobilin bonded to residue β158 overlaid with its calculated transition dipole (red arrow). The transition dipole was found as described in Section I using the above structure as input in TDDFT calculations. This image was generated using Visual Molecular Dynamics.[2]

Figure S5

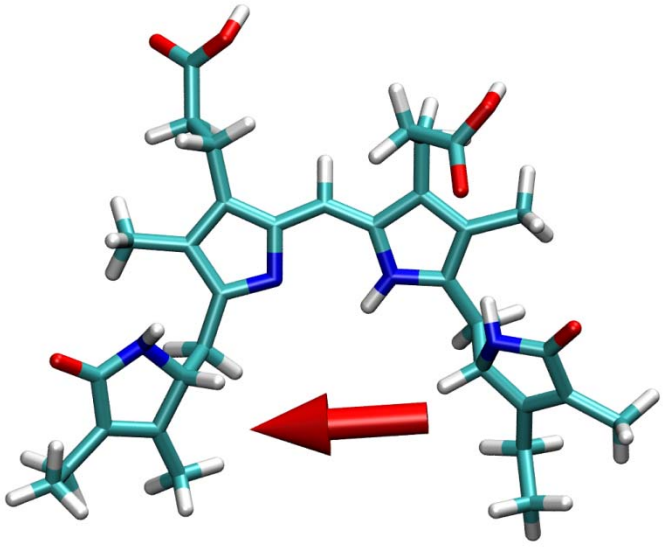

Figure S5. Structure of phycourobilin bonded to residue β50 and β61 overlaid with its calculated transition dipole (red arrow). The transition dipole was found as described in Section I using the above structure as input in TDDFT calculations. This image was generated using Visual Molecular Dynamics.[2]

Figure S6

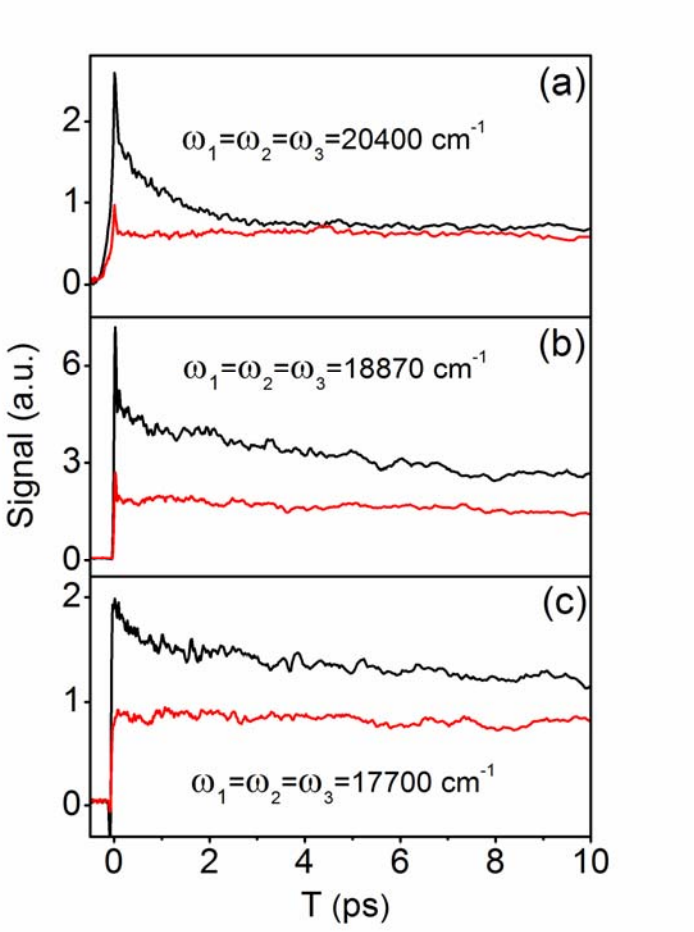

Figure S6. Absorptive parts of individual tensor elements, $S_{ZZZZ}(T)$ (black) and $S_{ZZXX}(T)$ (red), used to generate the anisotropies shown in Figure 7 of the main paper. Experiments are conducted in a one-color configuration, where the frequency corresponding to the peak of the laser spectrum is given in the figure legend.

References

(1) Dwyer, J.J.; Gittis, A.G.; Karp, D.A.; Lattman, E.E.; Spencer, D.S.; Stites, W.E.; García-Moreno, B.E. *Biophys. J.* **2000**, 79, 1610.

(2) Humphrey, W.; Dalke, A.; Schulten, K. *J. Molec. Graphics*, **1996**, 14, 33.