

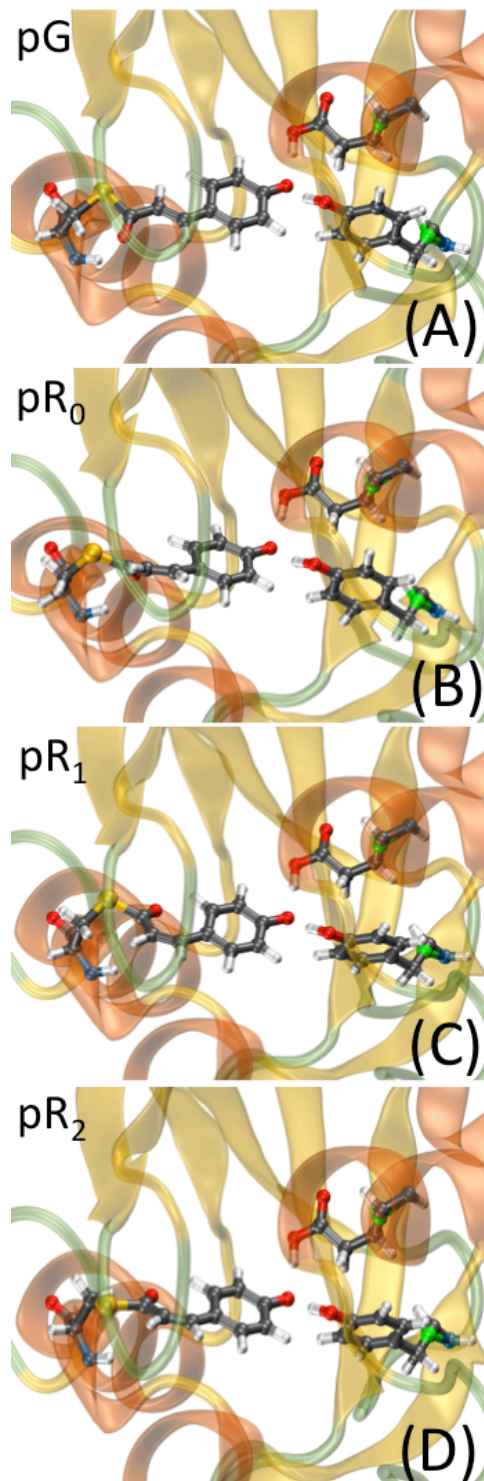
Supporting Information

Conversion of Light-Energy Into Molecular Strain in the Photocycle of the Photoactive Yellow Proteins

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Movie S1. QM/MM trajectories of the pCA chromophore in the four PYP photocycle intermediates (A) pG, (B) pR₀, (C) pR₁, and (D) pR₂. The figure shows the covalent bond between pCA and Cys-69, and the two hydrogen bonds to Tyr-42 and Glu-46.

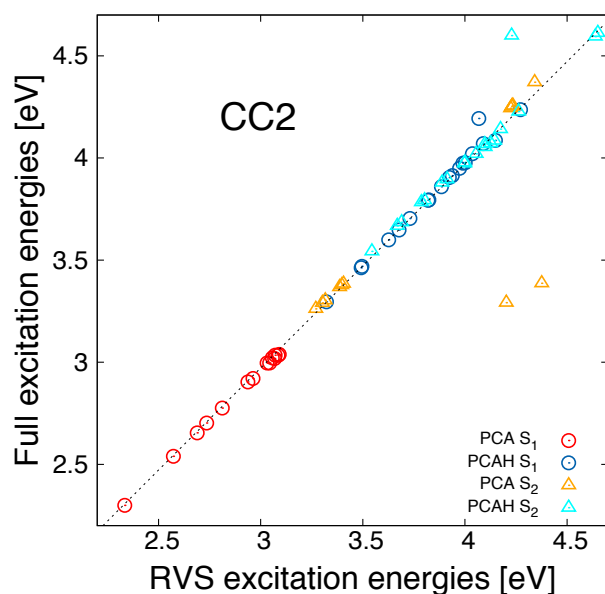


Figure S1. Comparison of CC2/def2-TZVP excitation energies (in eV) obtained using the frozen core approximation (FCI, Full excitation energies) and the FCI together with the restricted virtual space (RVS) approximation (RVS excitation energies). A cutoff value of 70 eV from the highest occupied molecular orbital (HOMO) was employed in the RVS approach. The values are calculated in vacuum along a scan of the C1-C2-C3-C1' dihedral rotation of the pCA chromophore. The discrepancy between the two approaches is ca. 0.02 eV (dashed line) for the first excited states (S1). For some S2 excited states the excitation character mixes, leading to higher RVS error for a few twisted geometries.

CAM-B3LYP vs CC2

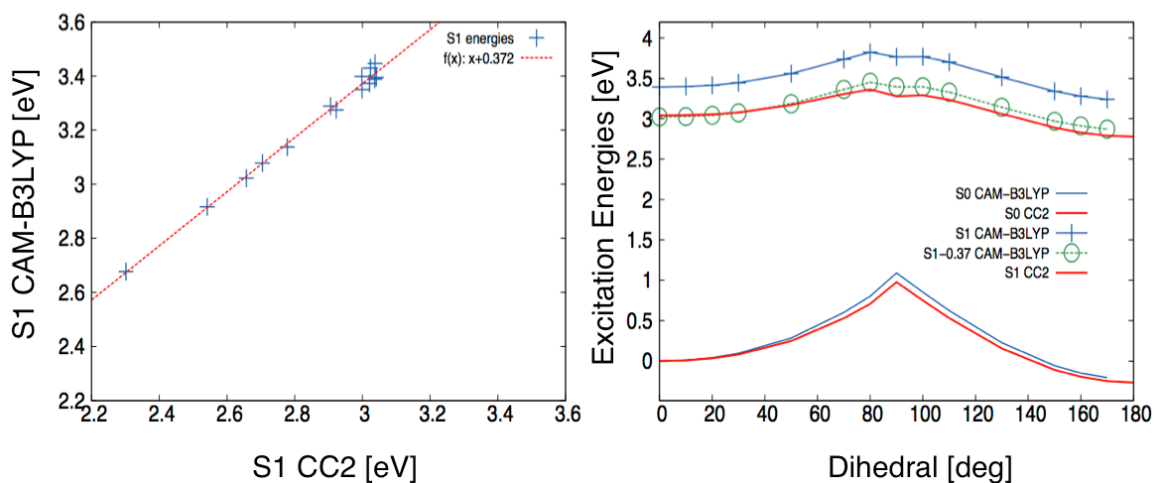


Figure S2. Left: CAM-B3LYP/def2-SVP and CC2/def2-TZVP predict similar trends for the excitation energies, but the former values are systematically blueshifted by ca. 0.37 eV (fitted line). Right: The energy profiles suggest that the S_1 excited state remains nearly constant with the dihedral twist, while the ground state (S_0) is strongly destabilized, leading to a large spectral shift.

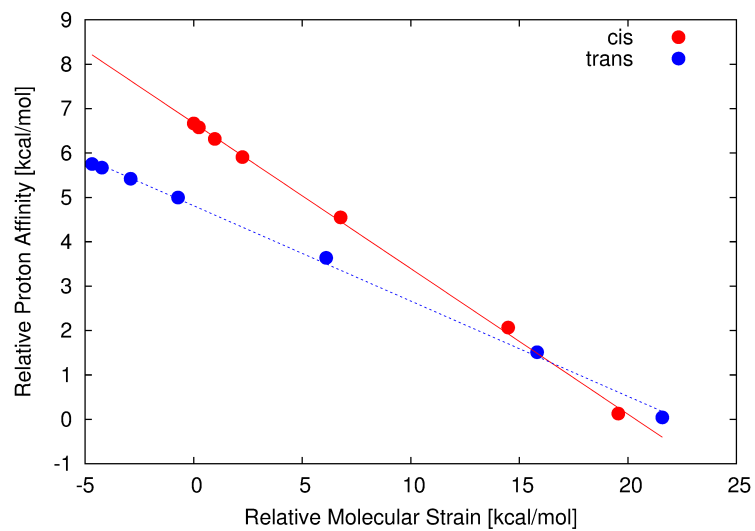
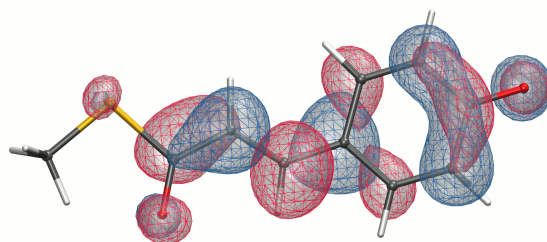


Figure S3. Twisting the C1-C2-C3-C1' dihedral angle of pCA increases the molecular strain of the chromophore, and increases the proton affinity by redistribution of electrons from the double bond to the phenolic group.



Movie S2. Highest occupied molecular orbital (in blue) and lowest unoccupied molecular orbital (in red) of the isolated pCA chromophore.

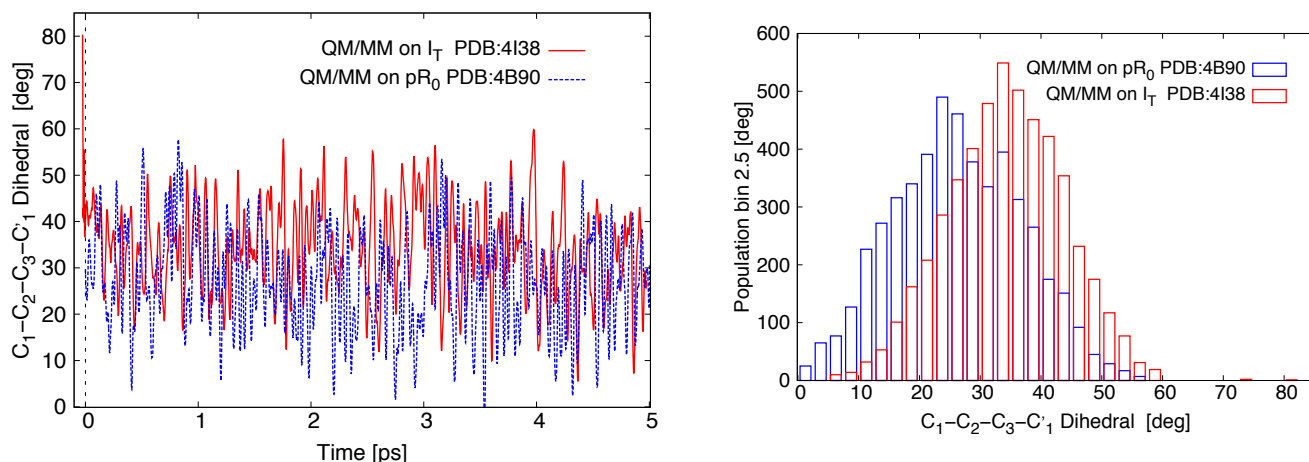


Figure S4. Comparison of the C1-C2-C3-C1' dihedral angle along 5 ps QM/MM MD simulation, using the X-ray structures reported by Jung *et al.*¹⁶ (PDB ID: 4I38) and Schotte *et al.*¹⁰ (PDB ID:4B90) as starting points. The I_T trajectory rapidly converges to a dihedral angle of $34 \pm 10^\circ$, consistent with the dihedral angle of 33° for the pR_0 structure of Schotte *et al.*, and the QM/MM simulations of the pR_0 state of $29^\circ \pm 18^\circ$. These results are consistent with the earlier DFT calculations by Kaila *et al.*¹¹

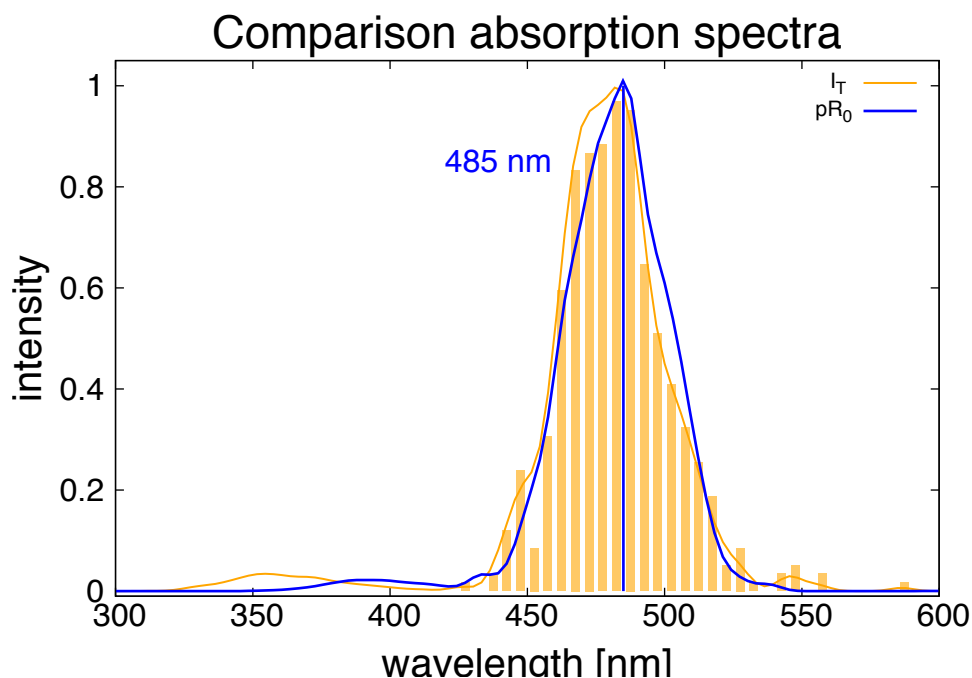


Figure S5. Ensemble averaged spectra of the I_T intermediate (yellow line) obtained from 5 ps QM/MM simulations using the X-ray structure reported by Jung *et al.* (PDB ID: 4I38)¹⁶ as a starting point. The figure also shows the spectra obtained from the pR_0 simulation (in blue). The spectrum was computed at CAM-B3LYP/def2-SVP level as a sum of Gaussians weighted by their respective oscillator strengths. The figure also shows the spectra of the I_T state calculated from histograms of the VEEs obtained from the QM/MM simulation (vertical bars).
