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Surface-enhanced photocycle studied in a single photoreceptor protein molecule KAAN KALKAN, AIHUA XIE, Oklahoma State University — Photoactive yellow protein (PYP) functions as a blue light sensor for bacterial vision (phototaxis). The photocycle of PYP is initiated by the absorption of a blue photon (absorption peak at 446 nm) by its para-coumaric acid (pCA) chromophore. The photon energy is stored in the pCA through photoisomerization which is subsequently transferred to the rest of the protein through a series of conformational states, finally leading to its partial unfolding (signaling). The present work captures the distinct conformational changes of PYP at the single molecule level, during the execution of its photocycle. In particular, the present work employs surfaceenhanced Raman scattering (SERS) active substrates and non-resonant excitation at 514 nm. As we confirm with regular Raman spectroscopy, the photocycle of PYP cannot be excited under 514 nm irradiation. On the contrary, 514 nm photons can excite the photocycle when PYP is adsorbed on silver, as we evidence from single molecule as well as ensemble-averaged SERS. In this case, the optical absorption of PYP shows a dramatic broadening (full width at half maximum shifting from 0.4to 0.9 eV) such that electronic excitation can occur significantly at 514 nm. Therefore, the origin of the observed "surface-enhanced photocycle" is understood to be of the same as "chemical enhancement" in SERS in view of the "adsorbate-induced resonance states" model (Persson, 1993).

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