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Photocycle of a single photoactive yellow protein molecule studied by surface-enhanced Raman scattering KAAN KALKAN, KUSHAGRA SINGHAL, WOUTER HOFF, AIHUA XIE, Oklahoma State University — We have demonstrated the detection of single molecules of photoactive yellow protein (PYP), by employing our novel surface-enhanced Raman scattering (SERS) active substrates. The Raman spectra reveal both "receptor" (G) and "signaling" (B) states of PYP at the single molecule level (at 514 nm excitation). The single molecule spectra are observed in terms of sudden appearance of discernable Raman peaks, each indicative of a PYP molecule finding a hot spot. The SERS spectra also exhibit various peaks, which are not normally Raman-active. Although the PYP has a long-lived signaling state (i.e., $\sim$0.3 s), the Raman peaks identifying this state are found to be dramatically narrow at the single molecule level for signal integration times of 0.25-0.5 s. In several instances, we observed subsequent change of the spectrum from B to G state. Although, the PYP is not chemisorbed on the metal nanoparticles, its short-term pysisorption is anticipated to allow for the capture of its photocycle at the single molecule level. In addition to narrower and better resolved peaks, the single molecule spectra also show variation in relative peak intensities. In particular, the C-C stretching and C-H bending modes of the aromatic ring of the chromophore inversely correlate at the single molecule level, while their intensities are comparable in the ensemble-average spectrum.

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