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Probing Blue Light Sensing Proteins with Ultrafast Spectroscopy and Chemical Biology

Light is essential to most life on earth, and most life forms developed tools for sensing light. In plants, bacteria and fungi a number of flavoproteins were recently shown to act as blue light sensors, alongside their established role in redox chemistry. Clearly the photochemical mechanism operating in these photoactive flavoproteins differs from that in light sensors such as rhodopsins, phytochromes and PYP, which undergo excited state isomerization reactions. In most cases we will see that the mechanism involves excited state electron transfer, sometimes ultrafast and sometimes involving the triplet state. The two flavoprotein families studied here – the Blue Light Using Flavin (BLUF) and Light-Oxygen-Voltage (LOV) domain proteins – exemplify both routes. The primary photochemical steps are probed by a combination of ultrafast electronic spectroscopy, excited state vibrational spectroscopy and mutagenesis. Of equal interest is how that primary event localized at the chromophore causes a structure change in the protein active sight, which is sometimes several nanometres away. Signal propagation pathways are investigated by transient IR spectroscopy coupled with chemical biology, especially the tools of non-canonical amino acid substitution.