Tracking Metalloprotein Dynamics at the Plastocyanin–Cytochrome *f* Interface with Infrared Probes

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A comprehensive understanding of photosynthetic metalloprotein electron transfer (ET) requires insight into how encounter-complex dynamics and the interfacial hydration network enable charge flow between metal sites. We focus on the interaction between cytochrome *f* (Cyt *f*) and plastocyanin (Pc) to probe how protein motions shape ET. In prior work, introducing C–D vibrational probes at the Pc Cu-site ligands Cys89 and Met97 revealed a pronounced change in the Cu–Cys89 interaction upon binding to Cyt *f*, indicating that ET-active metal sites are tuned not only within individual proteins but also by protein–protein complex formation. Here, we investigate how association with Cyt *f* remodels the inner coordination sphere of Pc's central copper when the Cu center is substituted with redox-active or redox-inactive metals (Figure 1). To assess how metal identity influences Pc–Cyt *f* association and ET, we employ site-specific C–D probes in infrared (IR) spectroscopy.

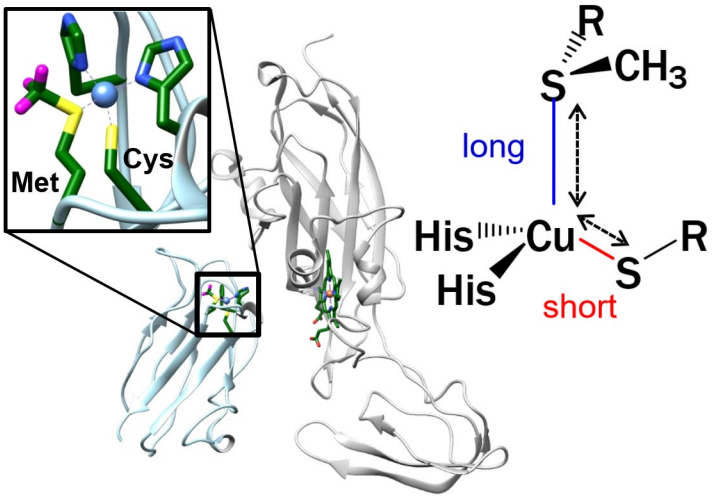

Figure. 1. Structure of the Pc (blue)–Cyt *f* (gray) complex (PDB *1TU2*). The inset highlights the plastocyanin Cu center (Cys/Met/His2 ligation). The diagram at right illustrates the characteristic distorted-tetrahedral geometry in blue-copper proteins: a short Cu–S(Cys) bond (red), a longer Cu–S(Met) interaction (blue), and two His ligands.