Bacteria like *Shewanella* and *Geobacter* are species that express multi-heme proteins which enable them to respire and survive without oxygen by reduction of extracellular solid substrates. Multi-heme proteins are fascinating biomolecules that bind several redox-active heme cofactors at close distance. They have attracted much attention recently due to their prominent role in mediating extracellular electron transport. Previously, our group has shown that electron transport through these structures occurs via electron hopping along the heme chains of the protein. In this work, I have used density functional theory (DFT) and molecular dynamics (MD) simulations to calculate all heme-to-heme electron transfer (ET) rate constants in three ubiquitous multi-heme proteins binding 4 and 10 heme cofactors, respectively. My calculations revealed that electron hopping through these proteins is strongly enhanced by cysteines that insert in the space between heme groups. We believe this to be a general design principle in multi-heme proteins for acceleration of ET steps that would otherwise be too slow for biological respiration. To verify our hypothesis and the computed rate constants, experimental collaborators docked a Ru-chromophore close to a terminal heme of one of the studied multi-heme proteins and used ultrafast pump-probe spectroscopy to monitor electron injection in the protein and subsequent relaxation dynamics. From these measurements, we could extract a heme-heme ET rate that is in good agreement with the results predicted from our computational approach.