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Probing electron-transfer pathways in cytochrome *c*

Previous studies of long-range electron transfer (ET) have shown the important role played by the intervening medium in determining the rate of the ET process. Electrons transfer through bonds much more favorably than they do through space. Calculations using the PATHWAYS model indicate that in yeast iso-1 cytochrome *c*, the electronic coupling between K72 and the heme iron is significantly greater than the coupling between the adjacent K73 and the heme iron. These calculations predict that ET from K72 to the heme will be faster than K73-to-heme ET under the same conditions. To test this prediction experimentally, we have prepared two single-histidine mutants of yeast iso-1 cytochrome *c* (H26N/H33N/H39Q/K72H/C102S and H26N/H33N/H39Q/K72A/K73H/C102S), which we are labeling with $[Ru(trpy)(bpy)(OH_2)]^{2+}$ (bpy = 2,2'-bipyridine, trpy = 2,2':6',2''-terpyridine). Rates of photochemically induced electron transfer in these Ru-modified proteins will be compared and discussed.