Photoinduced Multistep Tunneling in Azurin

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We are exploring multistep tunneling (hopping) through nitrotyrosines on the Cys112 arm of *Pseudomonas aeruginosa* azurin. We have synthesized and characterized high-potential ruthenium(II) sensitizers to couple to the histidines on the 112 strand (see below). We have attached $Ru(trpy)(flbpy)^{2+}$ to the His107 residue (flbpy = 4,4'-$(CF_3)_2$-bpy) and we are attempting to measure the rate of Cu(I) to Ru(III) electron transfer in a Ru(His107)(NO_2-Tyr108) derivative using a flash-quench method. Simulations based on tunneling timetables suggest that this electron transfer reaction will be greatly enhanced by hopping through the NO_2-Tyr108.

complex	MLCT	Emits at	Lifetime
$Ru(flbpy)_2(im)_2^{2+}$	514 nm	707 nm	34 ns
$Ru(trpy)(flbpy)(im)^{2+}$	494 nm	725 nm	46 ns
$Ru(trpy)(bpy)(im)^{2+}$	475 nm	695 nm	--
$Ru(4'\text{-}Cl\text{-}trpy)(bpy)(im)^{2+}$	480 nm	700 nm	--