The Role of Tryptophan and Tyrosine in Electron Transfer: Making and Measuring Radicals in the Model System Azurin

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It has been proposed that amino acid radicals play a role in long-range charge transfer in physiological (e.g., ribonucleotide reductase) and nonphysiological (e.g. DNA photolyase) pathways. If improving charge transfer pathways through enzymes can be as simple as introducing a few judicious mutations, the construction of biosensors that must transmit charge from an enzymatic active site to an electrode surface may be greatly facilitated. The ability of amino acids to enhance long-range charge transfer depends primarily on their oxidation potential, while the oxidation potential depends on the local environment of the amino acid.

To measure the range of oxidation potentials, we have placed individual tryptophan or tyrosine residues in at different places in azurin that feature different microenvironments. A solvent-accessible cysteine has been placed near the aromatic amino acid; this cysteine is then coupled directly to an alkanethiol monolayer that is attached to a gold electrode. This arrangement forms a direct wire from the electrode to the amino acid, allowing efficient electrochemical measurements. Preliminary measurements indicate that the relative ordering of the reduction potentials for tryptophan and tyrosine radicals free in solution is reversed from their values in the 108 position of azurin.