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Electron transfer oxidation of tryptophan and tyrosine by triplet states and oxidized radicals of flavin sensitizers: a laser flash photolysis study

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Abstract

The riboflavin (RF, Vitamin B_2) and flavin adenine dinucleotide (FAD)-sensitized photooxidation of tryptophan (TrpH) and tyrosine (TyrOH) were studied by laser flash photolysis. TrpH and TyrOH quench triplet flavin sensitizers to produce reduced flavin radicals (FlH$^{\bullet}$) and oxidized radicals of TrpH or TyrOH (Trp$^{\bullet}$ and TyrO$^{\bullet}$). Although Trp$^{\bullet}$ and TyrO$^{\bullet}$ cannot be observed directly by the laser flash photolysis, *N*,*N*,*N*â€²,*N*â€²-tetramethyl-*p*-phenylenediamine (TMPD), as a probe, was added to the system to result in the formation of radical cations of TMPD (TMPD$^{\bullet+}$) via quenching of Trp$^{\bullet}$ and TyrO$^{\bullet}$, which provides more definitive proof of electron transfer in the photosensitization

process than only direct observation of reduced flavin radicals. Electron transfer from TrpH and TyrOH to oxidized radicals of riboflavin and FAD with similar rate constants to the triplet flavins was observed for the first time, which may be a new way of TrpH and TyrOH damage. These results may shed new light on future application of flavins in photodynamic therapy, and imply that flavins might be applied potentially to photosensitization of oxygen deficiency or under high-intensity pulsed laser irradiation.

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Keywords

Flavin; Tryptophan; Tyrosine; Electron transfer; *N*,*N*,*N*â€²,*N*â€²-tetramethyl-*p*-phenylenediamine; Oxidized radical

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