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Fluorescent and photochemical properties of stable adducts of pyridoxal phosphate and other carbonyl compounds with hemoglobin and human serum albumin

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The reaction of pyridoxal phosphate (PLP) with apo-, oxy-, deoxyhemoglobin, human serum albumin (HAS) and amino acids under the action of UV and visible light at 4-37^{o}C at neutral pH gives rise to stable adducts, which withstand dialysis. The addition of electron acceptors like methylene blue, NAD^{+} and $NADP^{+}$ decreases the adduct formation rates for all samples. The adducts are strongly fluorescent and the fluorescence parameters are identical to those of the stable PLP adducts formed upon Schiff base (SB) reduction by $NaBH_4$. It is suggested that the photogenerated stable adducts are formed due to the reduction of the SB aldimine bond by light-ejected electrons. It is found that singlet oxygen is generated by free and reversible bound carbonyl compounds as well as by stable adducts with amino acids and proteins. The quantum yields of the photosensitized singlet oxygen generation for PLP, PLP-Val (Schiff base), PLP-Val (stable adduct) amount to 0.56, 0.31 and 0.13, respectively. The quantum yields 0.25 and 0.22 are obtained for PLP adducts with apohemoglobin and HAS, respectively. In the presence of effective electron donor a hydrogen atom of donor is captured by a molecule of carbonyl compound in a triplet state to produce a radical form. The unexcited molecule of carbonyl compound may play the role of electron donor. The semireduced compound transfers electron to oxygen to form a superoxide anion which is dismutated to hydrogen peroxide. The photodriven production of superoxide anions decreases the quantum yield of $^{1}O_2$ generation. For example, at concentration of $\geq 10^{-2}$ M pyruvate molecules generate superoxide only with the quantum yield of 0.76, whereas at lower concentrations they generate both $O^{\cdot -}{}_2$ and $^{1}O_2$. We suppose that PLP and its derivatives can be used as photosensitizer for photodynamic treatment of cancer.