DESIGN, SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF RECONSTITUTED MYOGLOBINS MODIFIED WITH C₆₀

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We describe herein the design, synthesis, and photophysical properties of myoglobin reconstituted with Fe- and Zn-protoporphyrins bearing C₆₀ (1•Fe-Mb and 1•Zn-Mb).¹

Fullerene-porphyrin conjugates (1•Fe and 1•Zn) were synthesized according to the literature² and reconstituted into apomyoglobin successfully to produce 1•Fe-Mb and 1•Zn-Mb, respectively (Figure 1). The axial-ligand exchange reaction indicated that 1•Fe-Mb possesses the intrinsic properties of native Mb except for the autodioxidation rate constant. Differential pulse voltamogram of a 1•Fe-Mb/tridodecylmethylammonium bromide film modified electrode in water containing 0.5 M tetraethylammonium chloride and 10 mM triethanolamine showed three cathodic peaks at E_{1/2, 1} = -0.38, E_{1/2, 2} = -0.56, and E_{1/2, 3} = -1.03 V which are attributable to Fe²⁺/³⁺, C₆₀⁰⁻, and the reduction of the porphyrin ring, respectively. The electrodes modified with 1•Fe-Mb/didodecyldimethyl-ammonium bromide (DDAB) and 1•Zn-Mb/DDAB gave anodic photocurrent coupled with on-off light irradiation. The action spectrum of photocurrent for a 1•Zn-Mb/DDAB film was in accord with the UV-visible absorption spectrum of 1•Zn-Mb. Transient absorption spectra of 1•Zn in benzonitrile and 1•Zn-Mb in a 50 mM phosphate buffer at 100 ns after the ns-laser light pulse irradiation at 532 nm showed three absorption maxima at 700, 830, and 1000 nm which are assignable to the triplet excited state of C₆₀ (C₆₀⁺), the triplet excited state of the Zn-porphyrin (1″ZnP⁺), and C₆₀ radical anion (C₆₀⁻⁻), respectively. Existence of the apparent C₆₀⁻⁻ indicates the generation of charge-separation state, ZnP⁺⁻⁻ C₆₀⁻⁻.


Figure 1. A schematic representation for 1•Fe-Mb.