DESIGN, SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF RECONSTITUTED MYOGLOBINS MODIFIED WITH C_{60}

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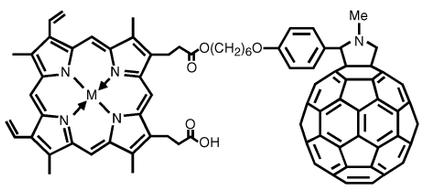
We describe herein the design, synthesis, and photophysical properties of myoglobins reconstituted with Fe- and Zn-protoporphyrins bearing C_{60} (**1**•Fe-Mb and **1**•Zn-Mb). [1]

Fullerene-porphyrin conjugates (**1**•Fe and **1**•Zn) were synthesized according to the literature[2] 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 the autoxidation rate constant. Differential pulse voltammogram 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 $Fe^{2+/3+}$, $C_{60}{}^{0/1-}$, 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 C_{60} ($^3C_{60}$*), the triplet excited state of the Zn-porphyrin (^{3}ZnP*), and C_{60} radical anion ($C_{60}^{\bullet -}$), respectively. Existence of the apparent $C_{60}^{\bullet -}$ indicates the generation of charge-separation state, $ZnP^{\bullet +}$- $C_{60}^{\bullet -}$.

1) H. Murakami, R. Matsumoto, Y. Okusa, T. Sagara, M. Fujitsuka, O. Ito, and N. Nakashima, *J, Mater. Chem.*, **12**, 2026-2033.

2) H. Murakami, Y. Okusa, S. Kiyonaka, I. Hamachi, S. Shinkai, and N. Nakashima, *Chem. Lett.*, **2000**, 46-47.



1•Fe (M = FeCl)
1•Zn (M = Zn)

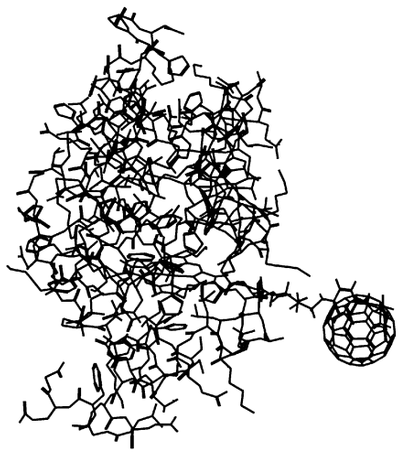


Figure 1. A schematic representation for **1**·Fe-Mb.