

## Supplementary Material

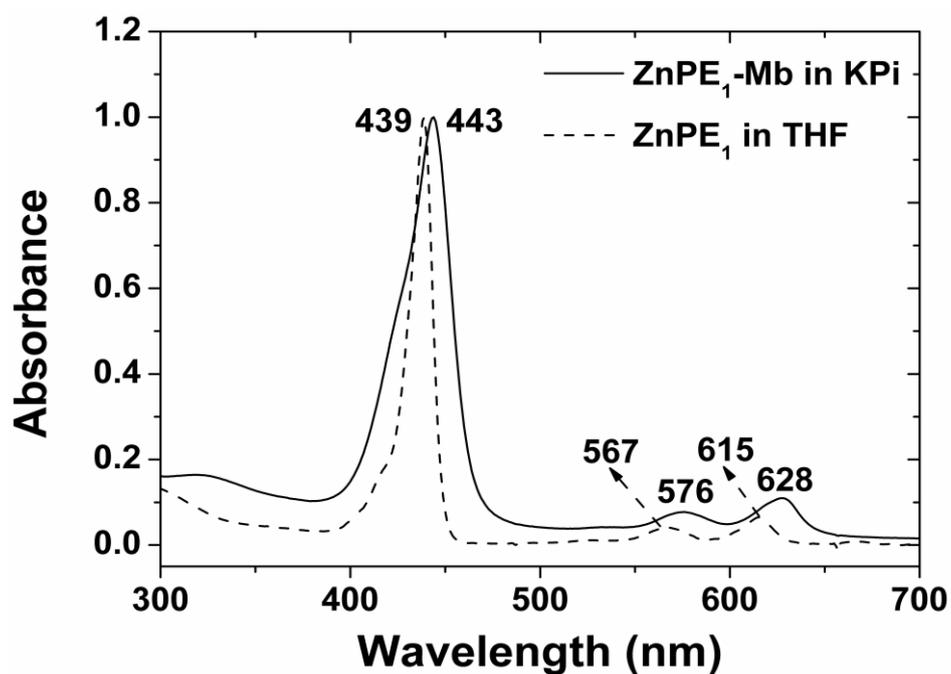
### Photoactivation Studies of Photoirradiated Zinc Porphyrin-Myoglobin System and Its Application for Light-Chemical Energy Conversion

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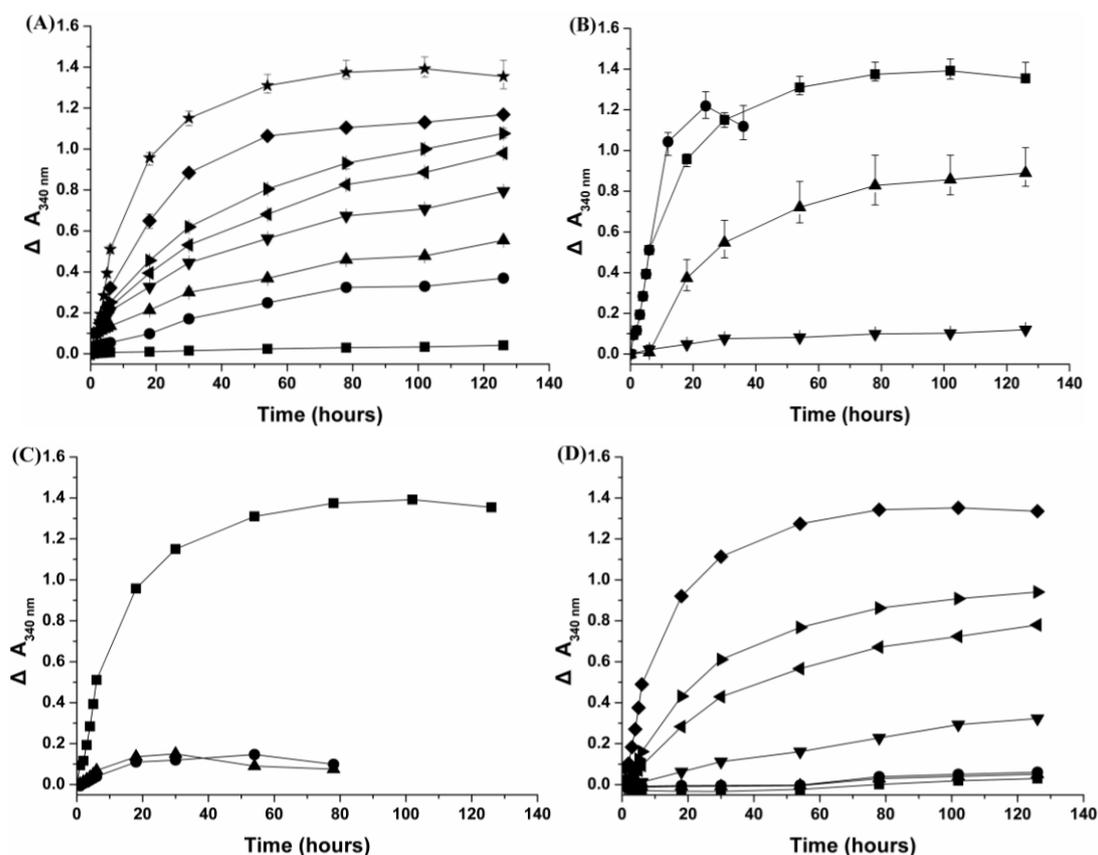
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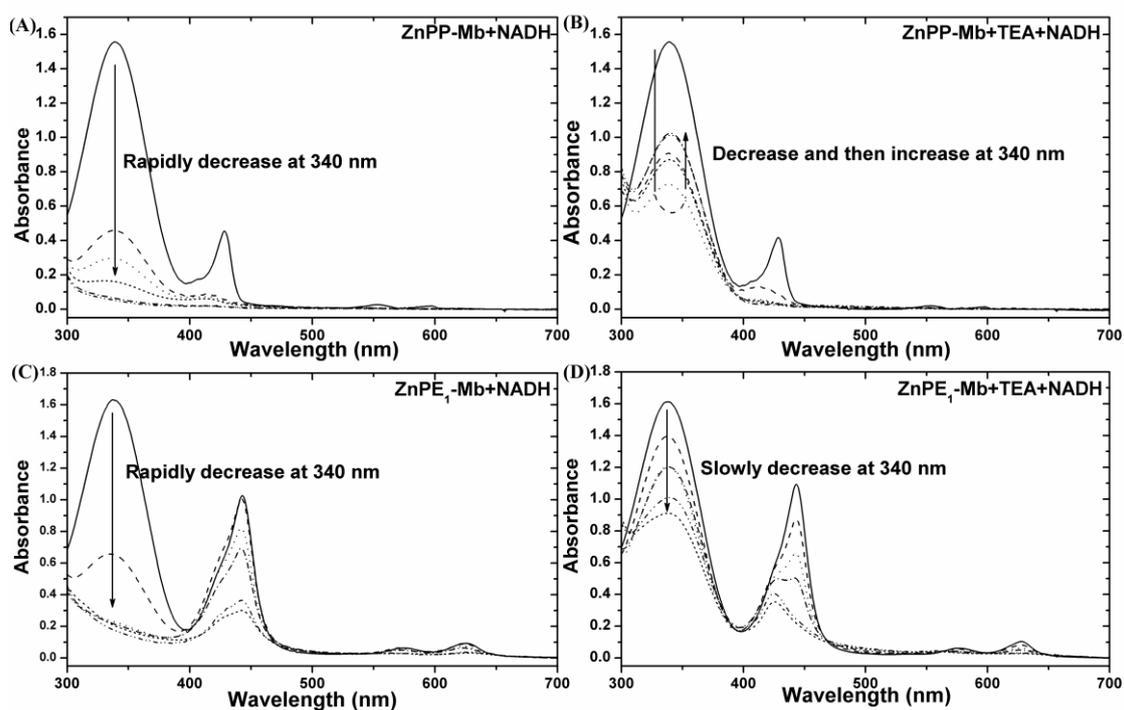
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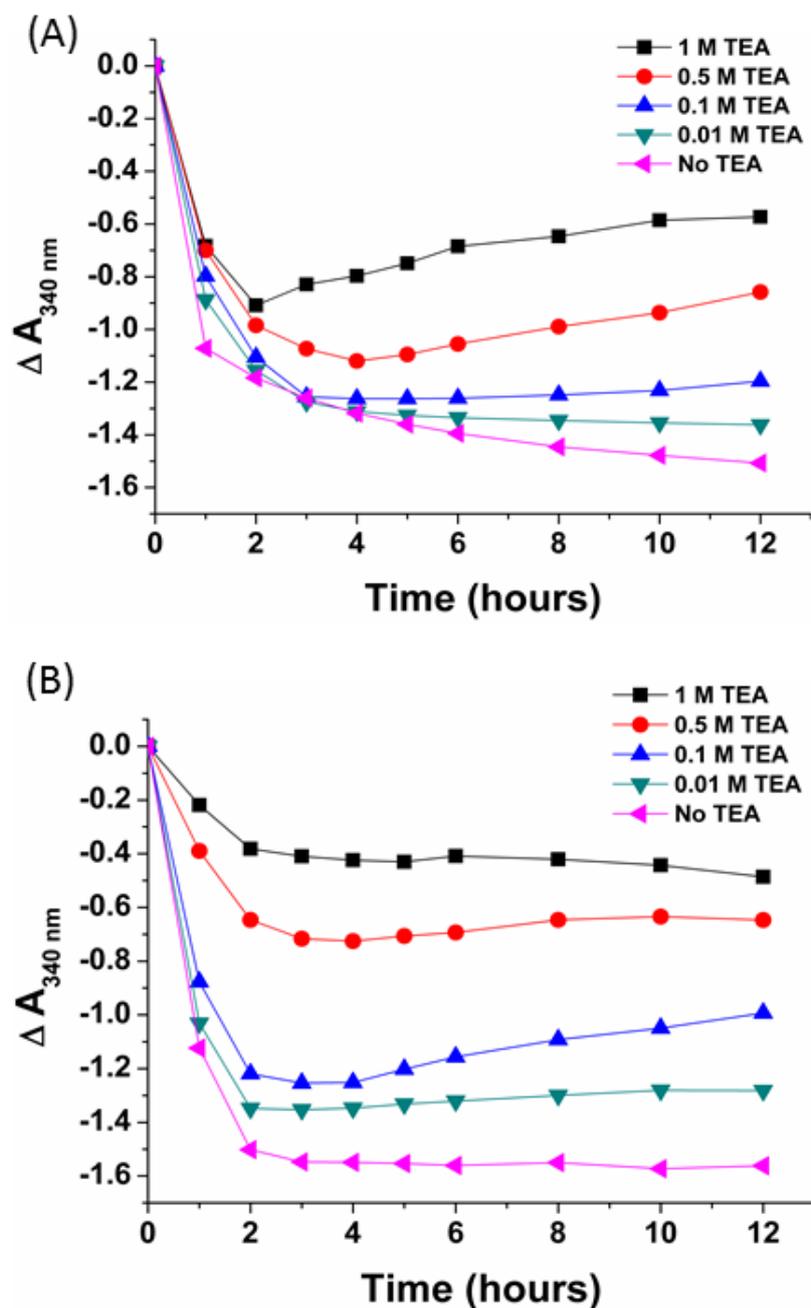
**Figure S1.** Steady-state absorption spectra of ZnPE<sub>1</sub> in THF (dash line) and ZnPE<sub>1</sub>-Mb in 100 mM KPi (solid line). Soret band of ZnPE<sub>1</sub> in THF is 439 nm and Q bands of ZnPE<sub>1</sub> in THF are 567/615 nm. Soret band of ZnPE<sub>1</sub>-Mb in 100 mM KPi is 443 nm and Q bands of ZnPE<sub>1</sub>-Mb in 100 mM KPi are 576/628 nm.



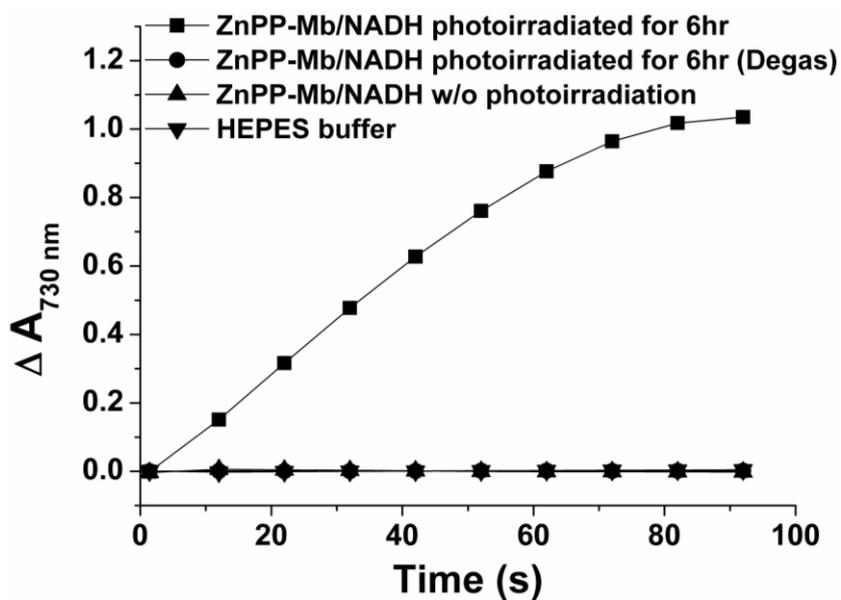
**Figure S2.** (A) Absorbance of 340 nm change for the solution containing ZnPP-Mb (25  $\mu\text{M}$ ), TEA (1 M), and NADP<sup>+</sup> (2.5 mM) irradiated by different duration (0 (■), 0.5 (●), 1 (▲), 2 (▼), 3 (◄), 4 (►), 5 (◆) and 6 (★) hours) then kept in dark. (B) Absorbance of 340 nm change for the solution containing ZnPP-Mb (25  $\mu\text{M}$ ), TEA (1 M), and NADP<sup>+</sup> (2.5 mM) under continued photoirradiation for 36 hours (●); 6 hours photoirradiation and dark reaction for 5 days (■); 6 hours photoirradiation (without NADP<sup>+</sup>) and dark reaction for 5 days (with NADP<sup>+</sup>) (▲), and continued dark reaction for 5 days (▼). (C) Absorbance change of photoirradiation by using ZnPP-Mb (25  $\mu\text{M}$ ) as a model photosensitizer, ethanolamines (MEA, DEA, and TEA, 1M) as sacrificial electron donor, and NADP<sup>+</sup> (2.5 mM) as substrate was irradiated for 6 hours then kept in dark. (D) Absorbance change in the solution containing 25  $\mu\text{M}$  of ZnPP-Mb, 2.5 mM of NADP<sup>+</sup>, and 0 (■), 1 (●), 10 (▲), 100 (▼), 250 (◄), 500 (►) and 1 M TEA (◆) was irradiated for 6 hours then kept in dark.



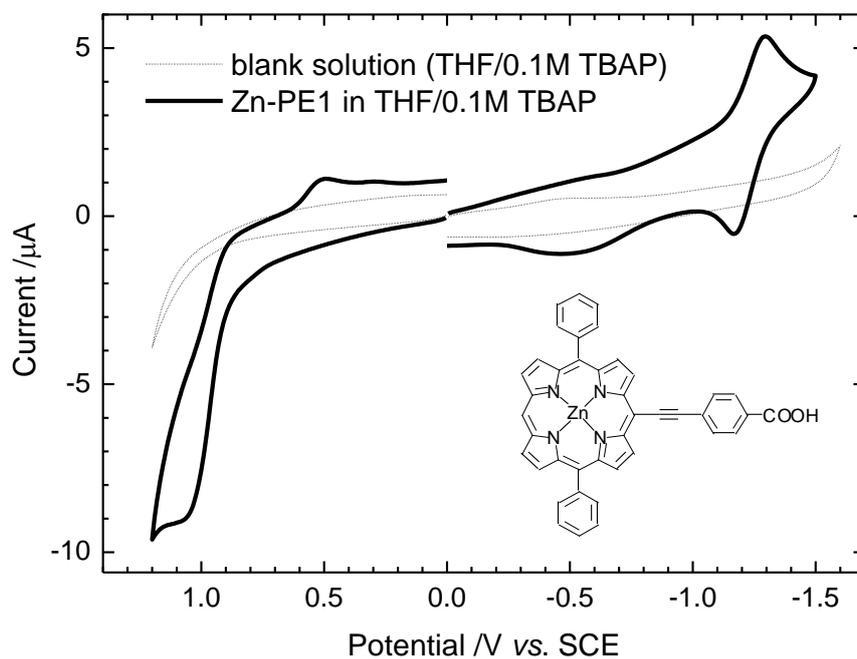
**Figure S3.** UV–visible spectral change under continued photoirradiation for 36 hr. (a) ZnPP-Mb + NADH, the absorbance at 340 nm was rapidly decrease and the Soret band at 428 nm was also decrease rapidly and a little blue-shift to 421 nm. (b) ZnPP-Mb + TEA + NADH, the absorbance at 340 nm was decrease at first two hours and then increase and Soret band at 428 nm was decrease and blue-shift to 413 nm. (c) ZnPE<sub>1</sub>-Mb + NADH, the absorbance at 340 nm was rapidly decrease and the Soret band at 443 nm was decrease gradually and no shift. (d) ZnPE<sub>1</sub>-Mb + TEA + NADH, the absorbance at 340 nm was slowly decrease and the Soret band at 443 nm was decrease gradually and blue-shift to 426 nm. [ZnPP-Mb] = 25  $\mu$ M, [ZnPE<sub>1</sub>-Mb] = 25  $\mu$ M, and [TEA] = 1 M and [NADH] = 2.5 mM. All in 20 mM HEPES (pH 8.5).



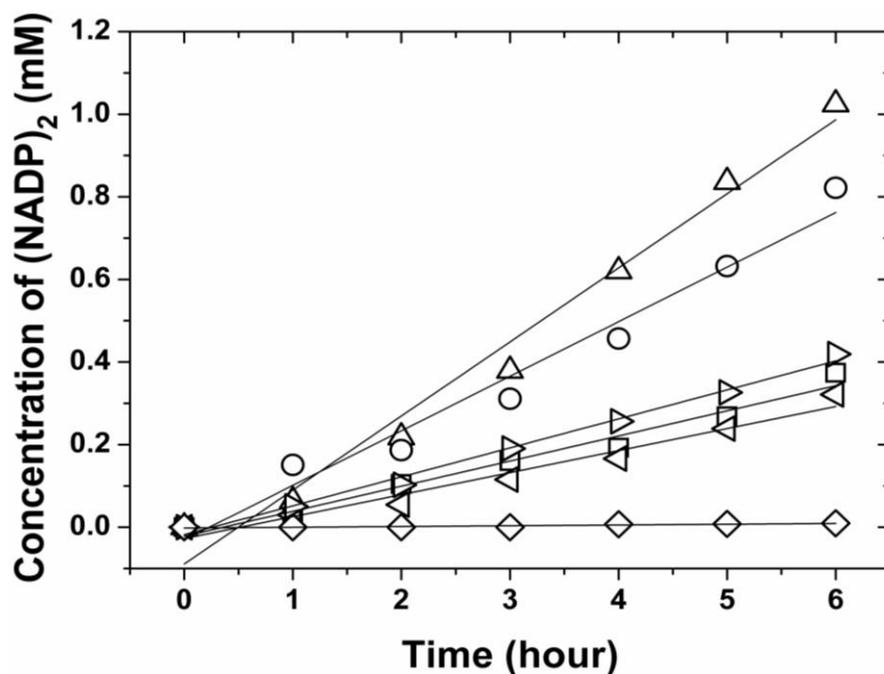
**Figure S4.** Concentration-dependent effect of TEA on (A) ZnPP-Mb + NADH + TEA and (B) ZnPE<sub>1</sub>-Mb + NADH + TEA photoirradiation reactions. (A) 25  $\mu\text{M}$  of ZnPP-Mb, 2.5 mM of NADH, and 1 (■), 0.5 (●), 0.1 (▲), 0.01 (▼), or 0 M (◄) of TEA was irradiated for 12 hours. (B) 25  $\mu\text{M}$  of ZnPP-Mb, 2.5 mM of NADH, and 1 (■), 0.5 (●), 0.1 (▲), 0.01 (▼), or 0 M (◄) TEA was irradiated for 12 hours.



**Figure S5.** Determination of  $\text{H}_2\text{O}_2$  following photoirradiation of ZnPP-Mb + NADH in the presence (■) or absence (●) of oxygen. [ZnPP-Mb] = 25  $\mu\text{M}$ , and [NADH] = 2.5 mM. All were in 20 mM HEPES (pH 8.5). The ZnPP-Mb + NADH without photoirradiation (▲) and HEPES buffer (▼) were used as negative control. The produced  $\text{H}_2\text{O}_2$  was incubated with 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) and peroxidase to generate a  $\text{ABTS}^{\bullet+}$  radical-cation, which can be monitored with absorbance at 730 nm.



**Figure S6.** Cyclic voltammogram of ZnPE<sub>1</sub> in THF. The first porphyrin-ring reduction was observed as a reversible reaction at -1.23 V vs. SCE and the first oxidation was observed as an irreversible reaction at +1.07 V vs. SCE. Experimental conditions: Zn-PE<sub>1</sub> (0.5 mM) in freshly distilled and degassed THF/0.1M TBAP, scan rate = 100 mV/s, Pt working and counter electrodes, SCE reference electrode.



**Figure S7.** Comparison of photosensitizer effect for catalytic kinetics at photoirradiation. 2.5 mM  $\text{NADP}^+$  with 1 M TEA were independently reacted with 25  $\mu\text{M}$  ZnPP-Mb (O), ZnPP (▷), ZnPE<sub>1</sub>-Mb (△), ZnPE<sub>1</sub> (◁) and ZnTMPyP<sup>4+</sup> (◻) under photoirradiation in 100 mM KPi, pH 9. 2.5 mM  $\text{NADP}^+$  with 1 M TEA reacted without photosensitizer (◊) was used as control.