## Supporting Information

# Development of Solar Cells Based on Synthetic Near Infrared Absorbing Purpurins: Observation of Multiple Electron Injection Pathways at Cyclic Tetrapyrrole-Semiconductor Interface

**Xiao-Feng Wang, Li Wang, Naoto Tamai, Osamu Kitao, Hitoshi Tamiaki and Shin-ichi Sasaki**

## S1. NMR Spectra for New Compounds

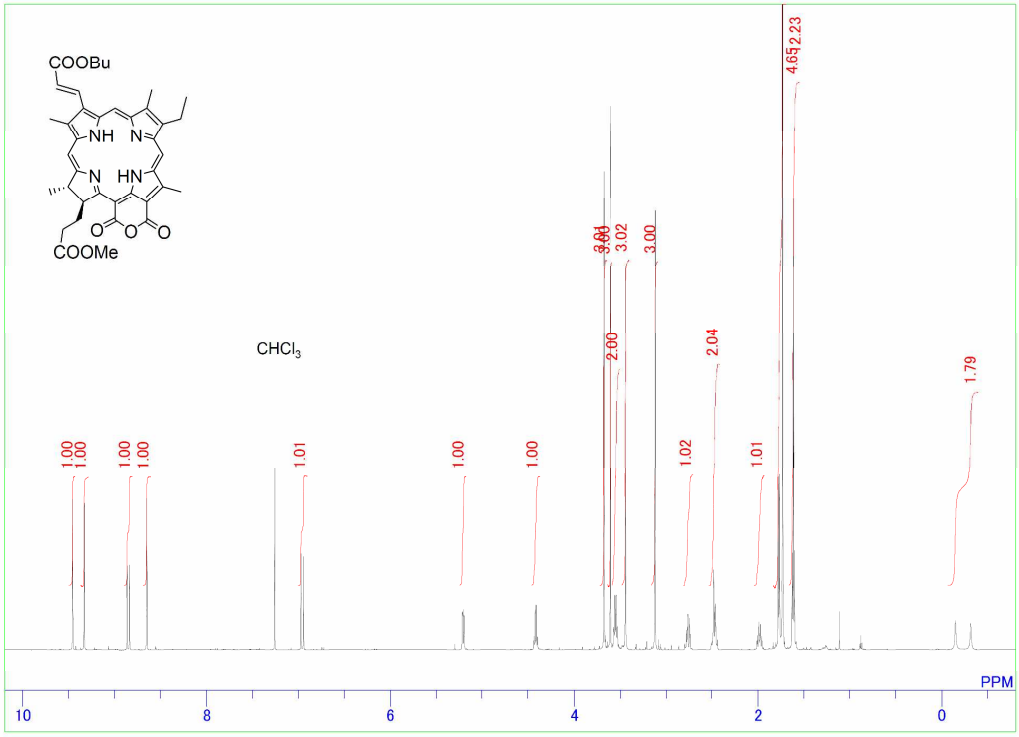


**Figure S1**. 600 MHz $^{1}$H-NMR spectrum of $\mathbf{H_2P}$ *tert*-butyl ester in $CDCl_3$.

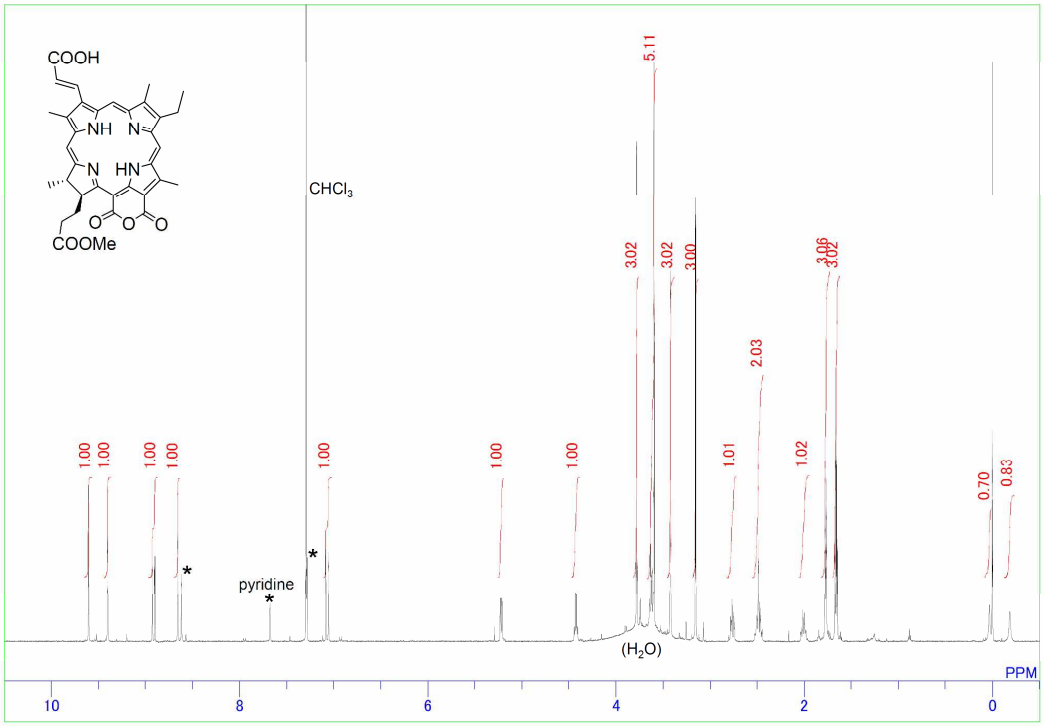


**Figure S2.** 600 MHz $^{1}$H-NMR spectrum of $\mathbf{H_2P}$ in 3% pyridine-$d_5$/$CDCl_3$.

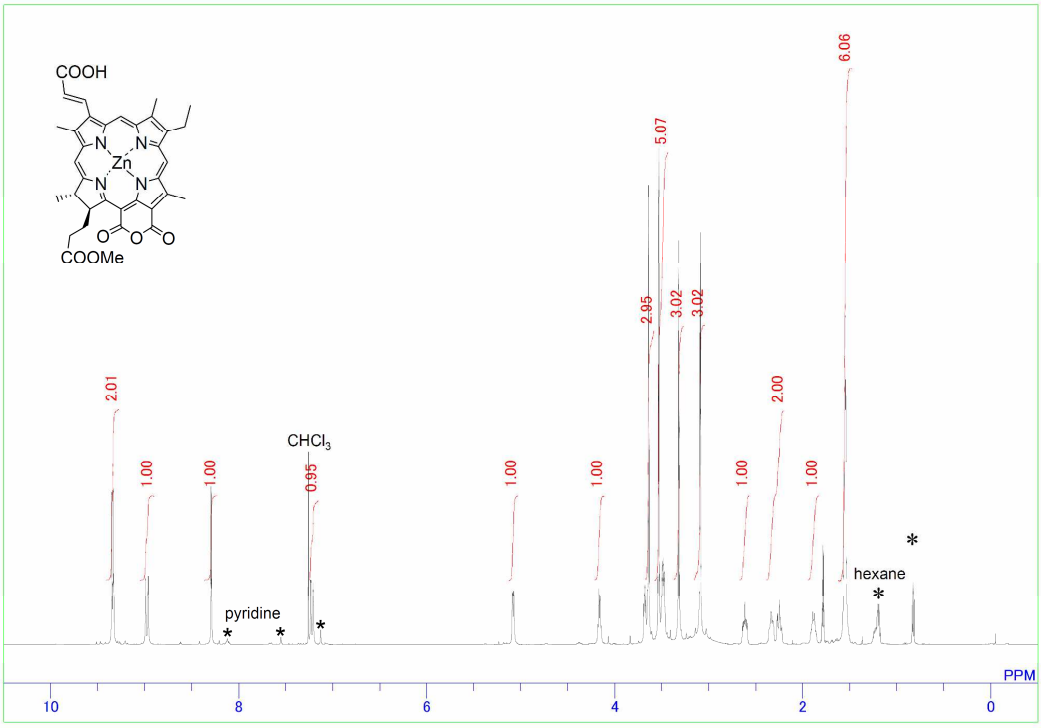


**Figure S3.** 600 MHz $^{1}$H-NMR spectrum of **ZnP** in 3% pyridine-$d_5$/$CDCl_3$.

**S2. Absorption Spectra of Dyes on Different Semiconductor Surface by TD-DFT calculation**

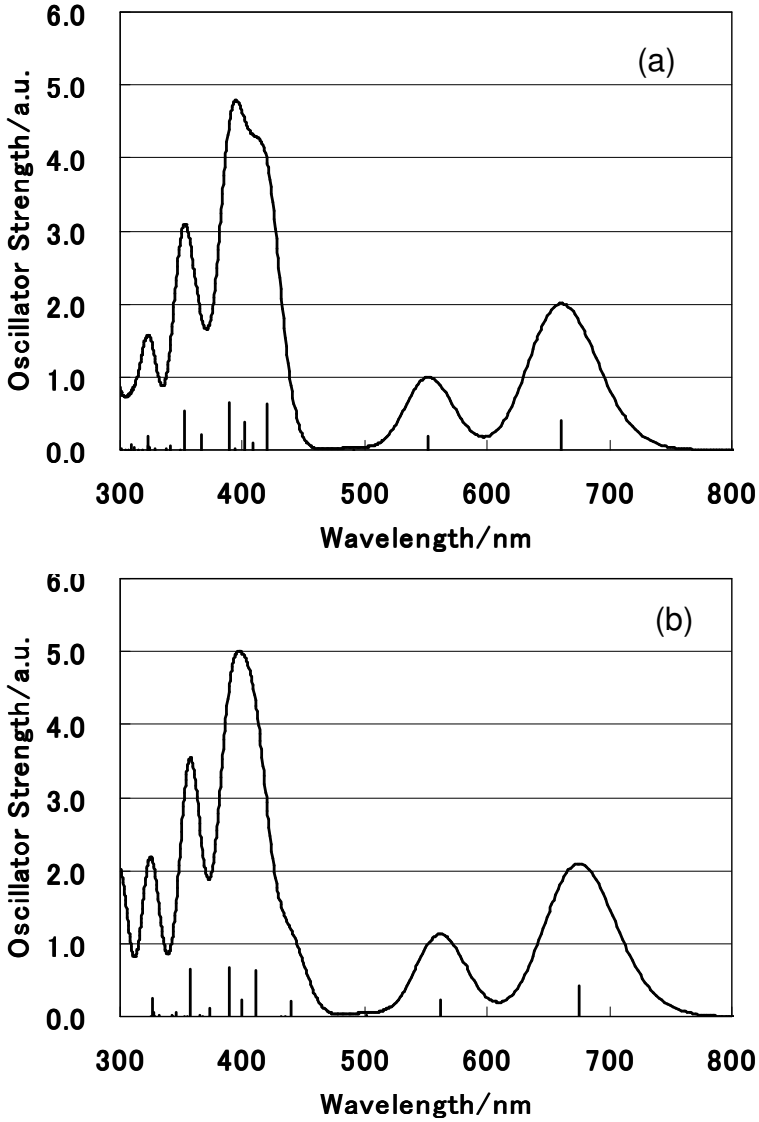


**Figure S4.** Calculated absorption energies and oscillator strengths based on TD-DFT/B3LYP/DGDZVP with CPCM (ethanol): (a) $\mathbf{H_2P}$-$TiO_2Na^+$; (b) $\mathbf{H_2P}$-$SnO_2Na^+$.

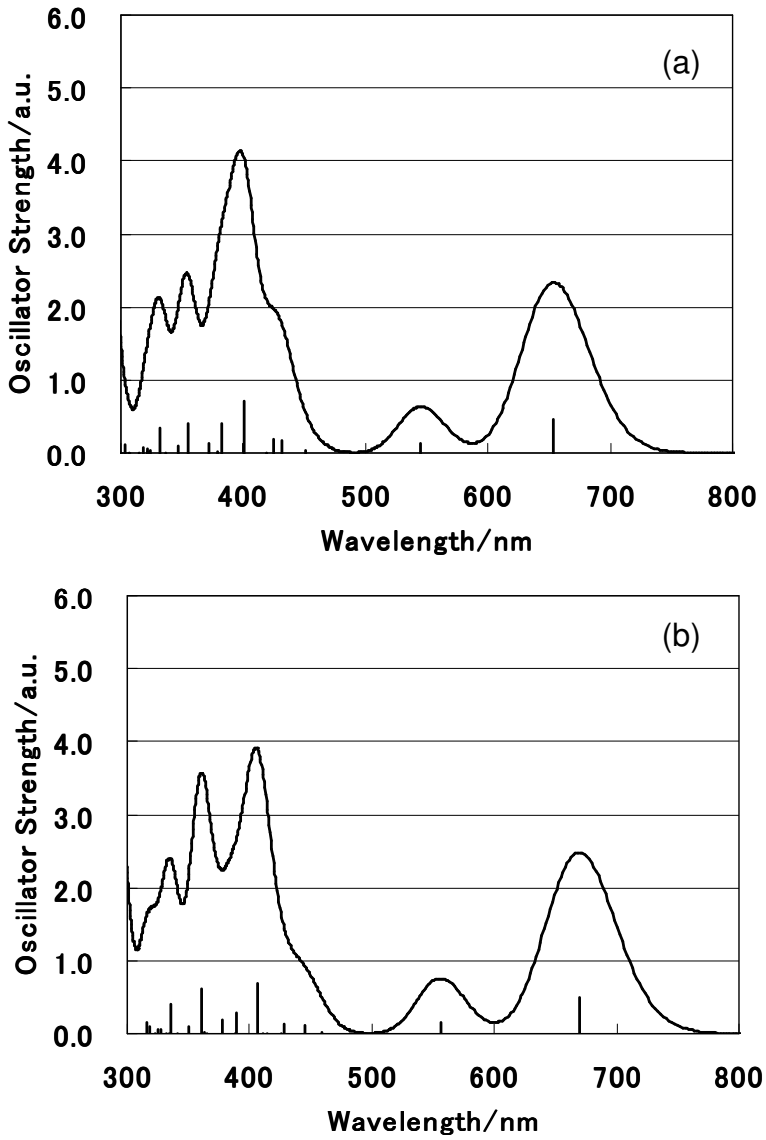


**Figure S5.** Calculated absorption energies and oscillator strengths based on TD-DFT/B3LYP/DGDZVP with CPCM (ethanol): (a) **ZnP**-$TiO_2Na^+$; (b) **ZnP**-$SnO_2Na^+$.

## S3. Measurement of HOMO Molecular Orbitals by Ultraviolet Photoelectron Spectroscopy

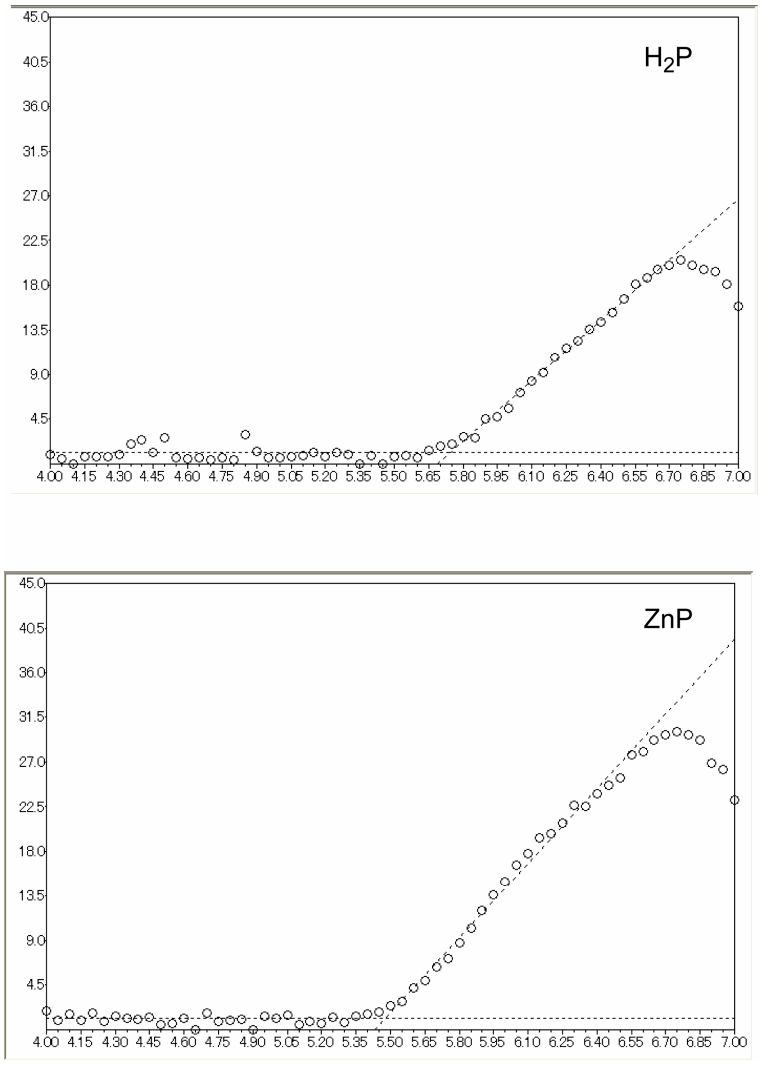


**Figure S6.** The Observed Energy of HOMO for **$H_2P$** and **ZnP** Deposited on $TiO_2$ Thin Films with AC-3, Riken Keiki Co.