Electronic Supplementary Information

Zn-Containing Porphyrin as a Biomimetic Light-Harvesting Molecule for Biocatalyzed Artificial Photosynthesis

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MATERIALS & METHODS

Materials: Tetrakis(4-sulfonatophenyl)porphyrin (TPPS), Zn(II)TPPS, Mn(III)TPPS, Tetrakis(4-carboxyphenyl)porphyrin (TPPC), Zn(II)TPPC, and Mn(III)TPPC were purchased from Frontier Scientific, Inc (Logan, UT). NAD^+, triethanolamine (TEOA), α-ketoglutarate, ammonium sulfate, and glutamate dehydrogenase (GDH) were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used without further purification. **M** was synthesized according to the literature (Lee et al., 2009).

Photochemical NADH regeneration using various porphyrins: The NADH regeneration was performed in a quartz reactor in an Ar atmosphere at room temperature. 1 mM NAD^+ and 0.5 mM **M** were dissolved in a degassed phosphate buffer (100 mM, pH 7.5) containing 15 w/v% TEOA. Under Ar atmosphere, degassed phosphate buffer can prevent the oxidation of NADH to NAD^+ (Donk and Zhao, 2003). We then dissolved 0.5 mM porphyrin in the reaction solution, which was then exposed to the light from a 450 W Xe research arc lamp source (62 mW cm^{-2}) with a 400 nm cut-off filter. The concentration of NADH was measured by analyzing its absorbance at 340 nm with a spectrophotometer (Biospec Mini, Shimadzu Co., Japan).

Biocatalytic L-glutamate synthesis coupled with NADH regeneration using various porphyrins: For the photosynthesis of L-glutamate, we conducted the reaction with 1 mM NAD$^+$, 0.5 M **M**, 1 mM α-ketoglutarate, 100 mM ammonium sulfate, and 40 U GDH, based on a degassed phosphate buffer (100 mM, pH 7.5) with 15 w/v% TEOA. To avoid any side reaction such as a reaction between α-ketoglutarate and singlet oxygen produced by porphyrin (Jefford et al., 1976; Scalise & Durantini, 2004), 0.5 mM porphyrin was dissolved under Ar atmosphere in the reaction solution, which was then exposed to the light from the 450 W Xe research arc lamp source (62 mW cm^{-2}) with a 400 nm cut-off filter. To quantitatively estimate the concentration of L-glutamate, high-performance liquid chromatography (LC-20A prominence, Shimadzu Co.,) equipped with an Inertsil C18 column (ODS-3V, length, 150 mm) was used. Samples were eluted by phosphoric acid (0.05%) with flw rate of 1.0 mL min^{-1} detected at 214 nm.

*Characterization of the energetic relationship between porphyrins and **M***: Spectrofluorometric experiments were performed with the RF-5301PC (Shimadzu Co., Japan). The emission spectra were measured under an excitation wavelength of 400 nm. A 3-electrode system was used to obtain a linear sweep voltammogram; a glassy carbon disk (working electrode), Ag/AgCl (reference electrode, 0.197 V versus normal hydrogen electrode), and a platinum wire (counter electrode) were connected to a multi channel potentiostat/galvanostat (WonATech, Model WMPG1000, Korea) with a 100 mV s^{-1} scan rate. Fourier-transform infrared (FT-IR) spectra of samples were collected using a JASCO FT-IR-6100 spectrometer (JASCO Inc., Tokyo, Japan) at a resolution of 2 cm^{-1} under vacuum.

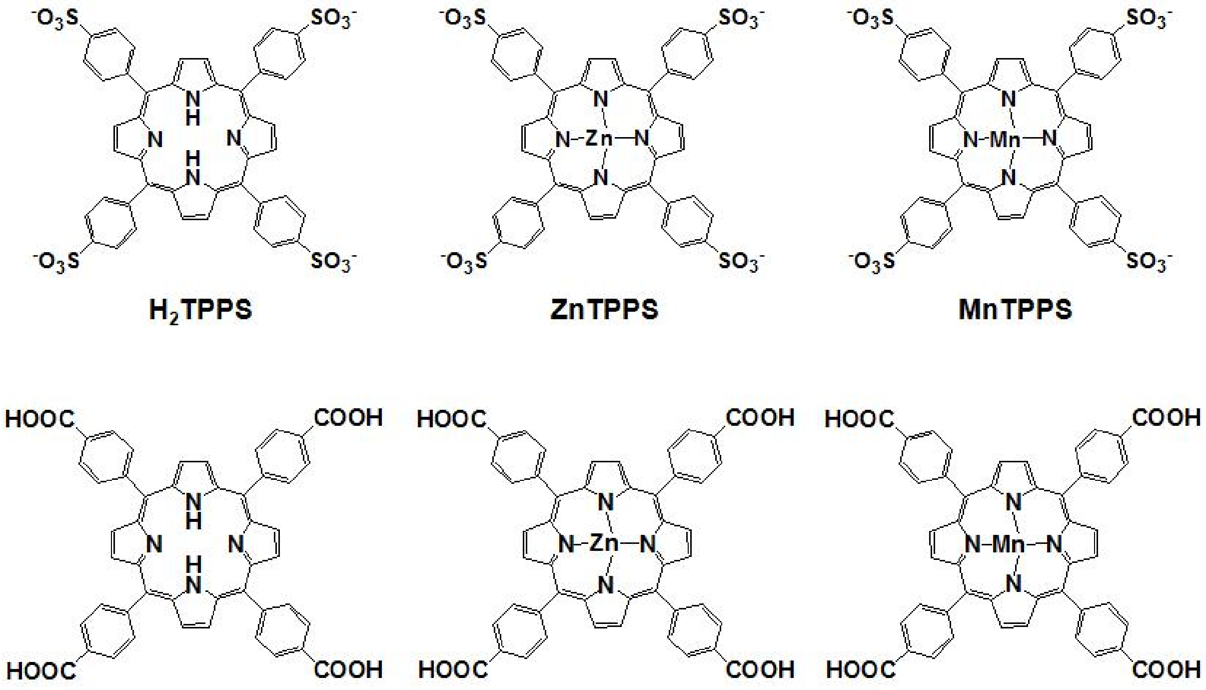

Figure S1. Molecular structure of porphyrin molecules having different metal insertion sites (e.g., no metal, Zn, or Mn) and functional ligands (e.g., sulfonato or carboxyl group).

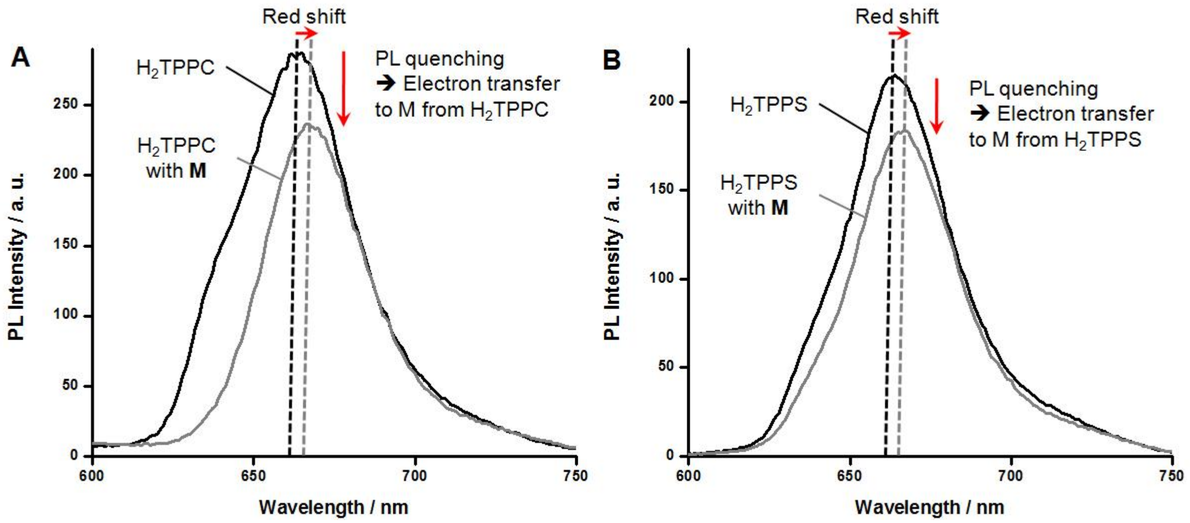

Figure S2. The change in emission spectrum for (A) H_2TPPC and (B) H_2TPPS without **M** (black line) and with 0.125 mM **M** (gray line).

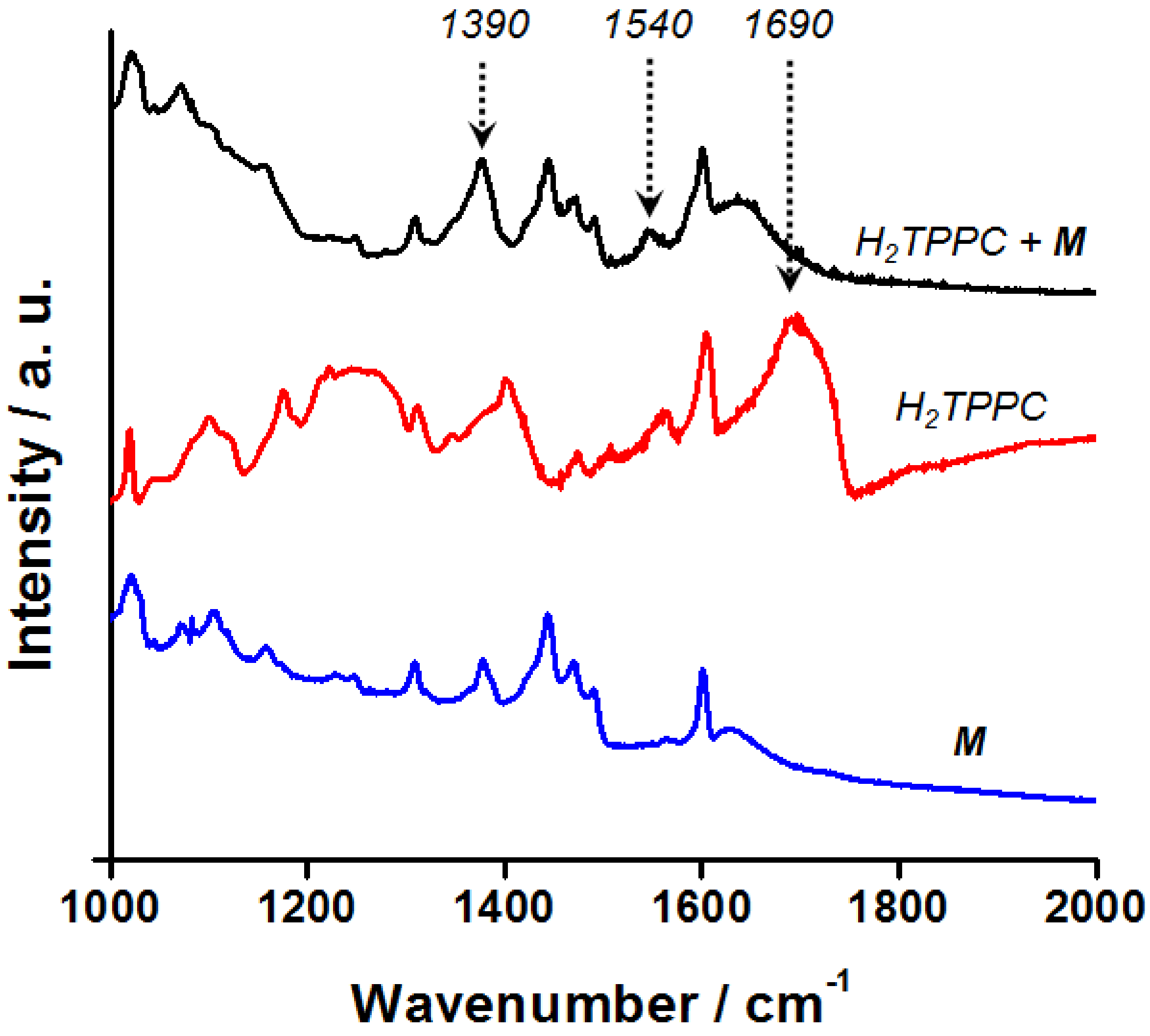

Figure S3. FT-IR spectra of H_2TPPC, **M**, and H_2TPPC + **M**. The v(C=O) and v(C-O) stretching modes at 1690 cm^{-1} of H_2TPPC was siginificantly suppressed by the addition of **M**. At the same time, the v(CO_2^-) stretch in the mixture was higher than **M** without H_2TPPC at 1390 cm^{-1}. It suggests that H_2TPPC was consistent with chelating or bidentate binding to the **M** like H_2TPPC-TiO_2 composites. (Rochford et al., 2007)

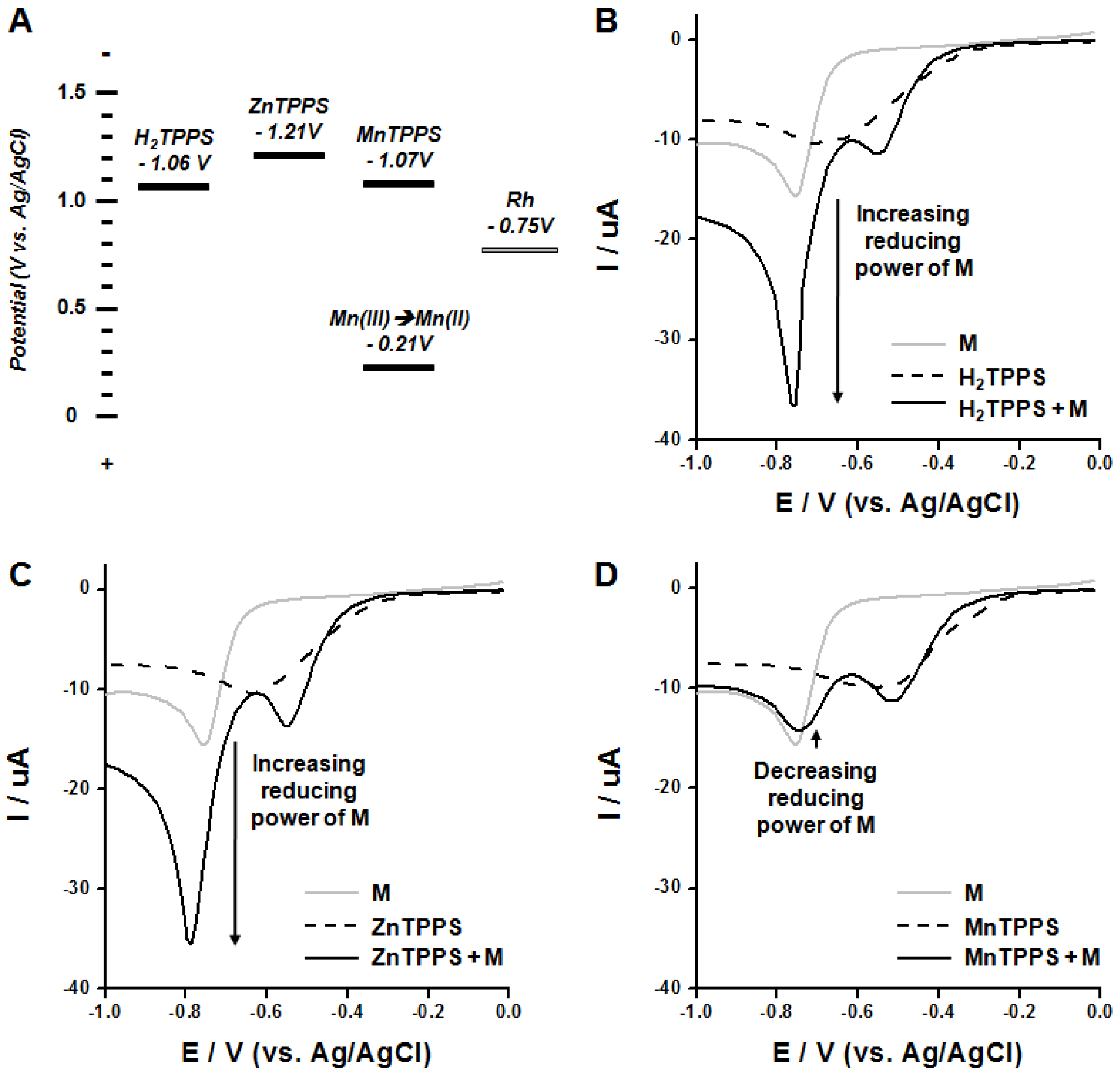

Figure S3. Energetic relationship between the TPPS group and **M**. (A) Reduction potential of porphyrin (H_2TPPS, ZnTPPS, MnTPPS) and **M**. Linear sweep voltammograms for **M** with or without (B) H_2TPPS, (C) ZnTPPS, and (D) MnTPPS. The potential was scanned at 100 mV s^{-1}.

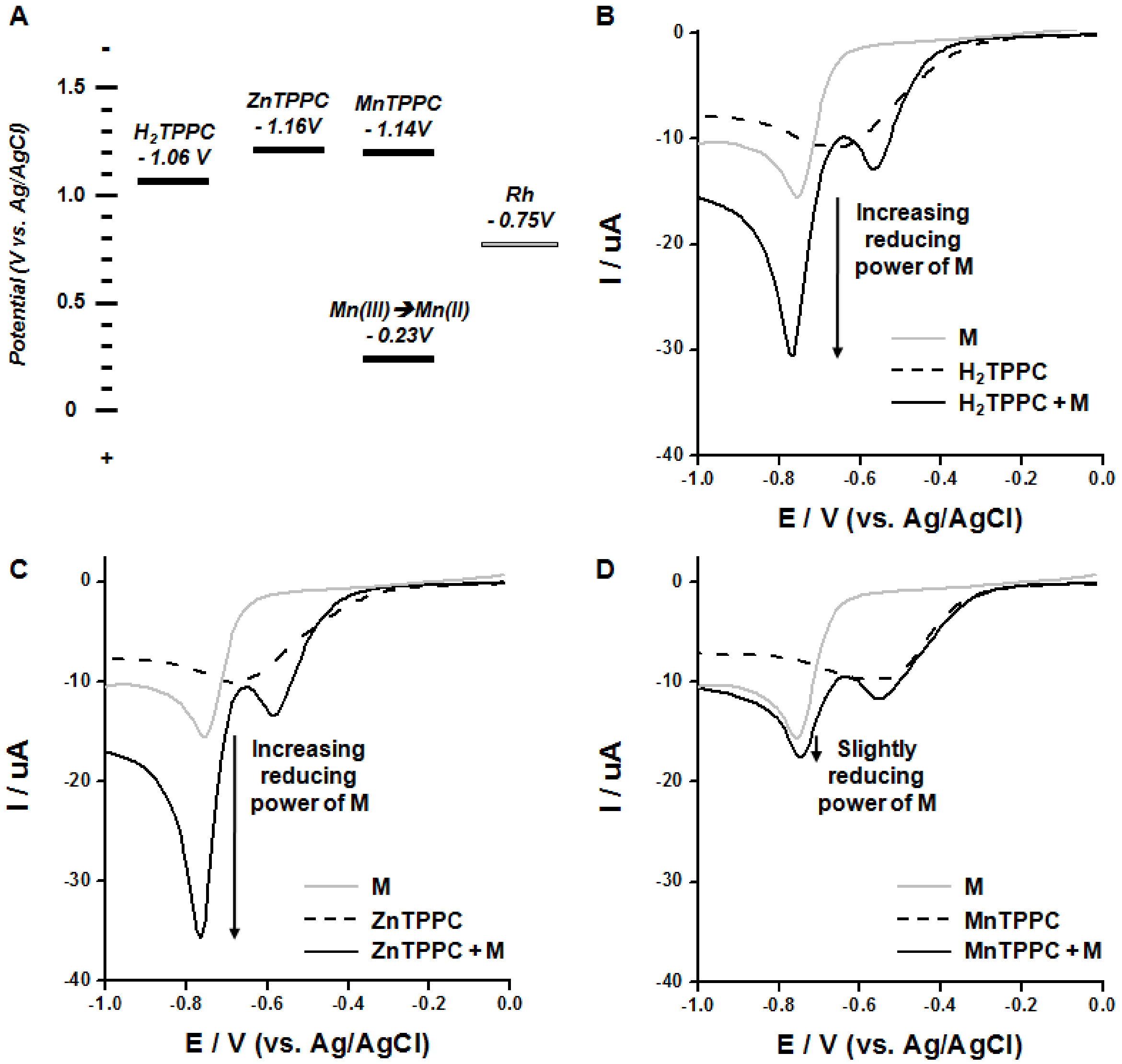

Figure S4. Energetic relationship between the TPPC group and **M**. (A) Reduction potential of porphyrin (H_2TPPC, ZnTPPC, MnTPPC) and **M**. Linear sweep voltammograms for **M** with or without (B) H_2TPPC, (C) ZnTPPC, and (D) MnTPPC. The potential was scanned at 100 mV s^{-1}.

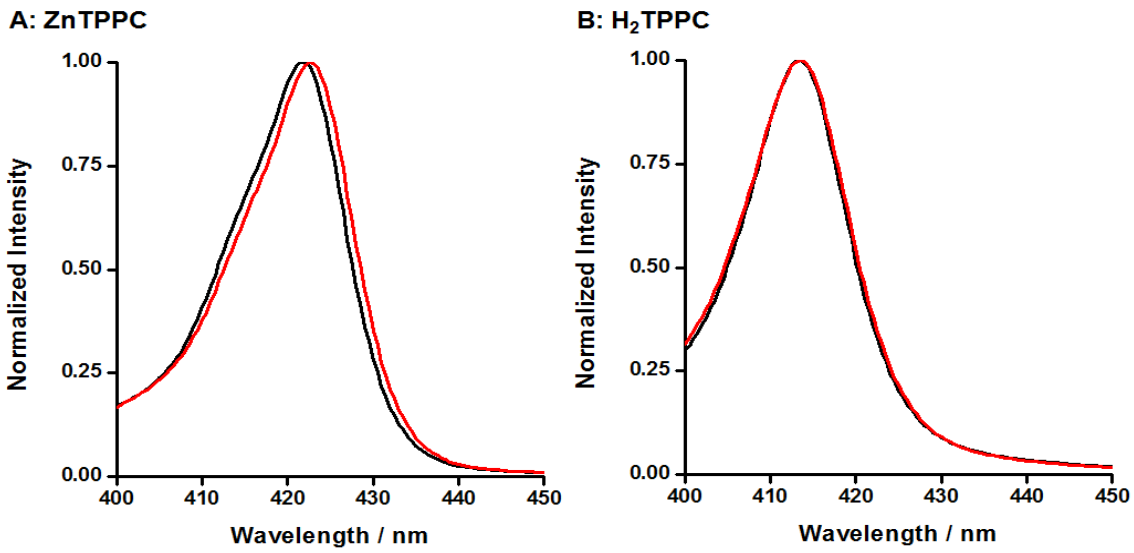

Figure S5. Absorbance spectrum for (A) 0.1 μM ZnTPPC and (B) 0.1 μM H_2TPPC with (red line) or without (black line) 0.1 mM TEOA.

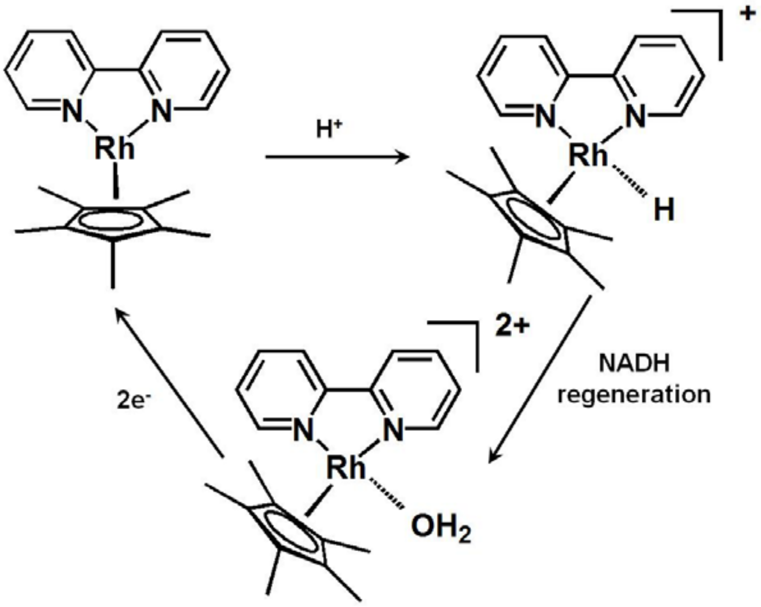

Figure S6. Molecular structures of three different electrochemical states of **M** and indirect NADH regeneration by **M** (Stekhan et al., 1991; Lo et al., 2001).

References for Electronic Supplementary Information

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