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Supporting Information

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DOI: 10.1002/cbic.200900156

Supporting Information

for

Eosin Y-Sensitized Artificial Photosynthesis by Highly Efficient Visible-Light Driven Regeneration of Nicotinamide Cofactor

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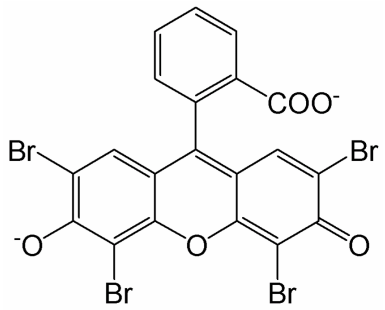

Figure S1. Chemical structure of Eosin Y

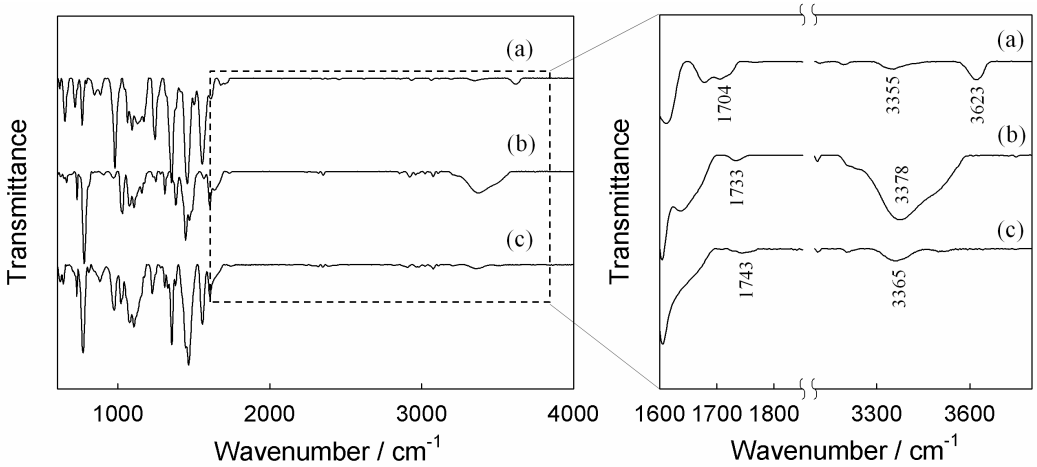

Figure S2. FT-IR spectra of Eosin Y (a), **M** ($[Cp^*Rh(bpy)H_2O]^{2+}$) (b), and a mixture of the two components (c). A peak corresponding to carboxyl C=O stretch of Eosin Y shifted from 1704 cm^{-1} (in (a)) to 1743 cm^{-1} (in (c)) by the addition of **M,** implying that the C=O stretch of Eosin Y carboxylic group is restricted by Rh-O bond in Eosin Y-**M** complex. At the same

time, the O-H stretch of H_2O (3378 cm^{-1}) present in **M** was significantly suppressed by the addition of Eosin Y (3365 cm^{-1}). It suggests that H_2O moiety in **M** was exchanged by Eosin Y. Also, the suppression of phenolic O-H stretch in Eosin Y (3623 cm^{-1}) implies that the Rh-O bond between Eosin Y and **M** is available through both carboxylic and phenolic groups of Eosin Y.

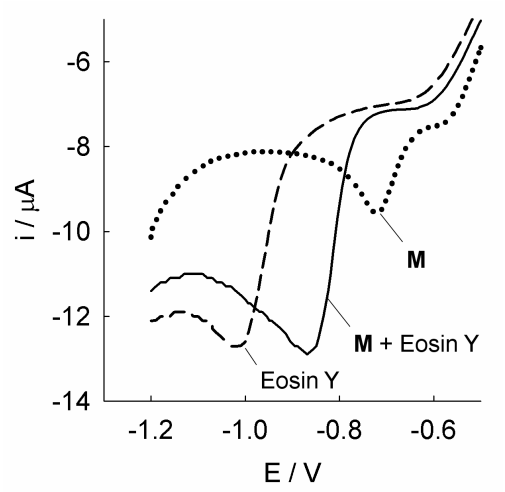

Figure S3. Linear sweep voltammograms of **M** (0.5 mM, -0.729 V) and Eosin Y (1 mM, –1.02 V) solutions on a glassy carbon disk electrode. Samples were prepared in a phosphate buffer (50 mM) at pH 7.0. The scan rate was 50 mVs^{-1}. A clear shift of reduction peak potential is observed in the mixture of **M** and Eosin Y (**M** + Eosin Y, -0.869 V) compared to the potentials of single compartments. This observation strongly supports the findings of Figure 4a and 4b in the main text.

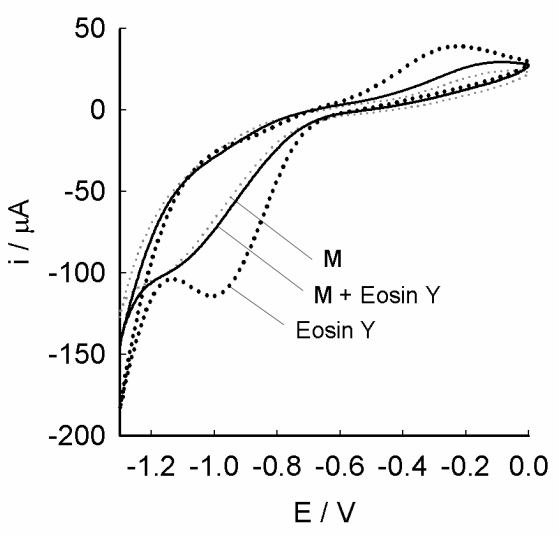

Figure S4. Cyclic voltammograms of **M** (0.25 mM) and Eosin Y (0.05 mM) solutions on an Au disk electrode. Samples were prepared in a phosphate buffer (100 mM) at pH 7.0. The

scan rate was 100 mVs^{-1}. In contrast to the slight change of the cyclic voltammogram of **M** on a GC electrode, the voltammogram of EY showed more drastic changes on an Au electrode. Both cathodic (-1.0 V vs. Ag/AgCl) and anodic (-0.3 V vs. Ag/AgCl) peaks of EY disappeared with the addition of **M**. The shift of the reduction peak of **M** on a GC electrode, as well as the suppressed redox behavior of EY on an Au electrode, indicate that **M** functions as a primary electron acceptor in the EY-**M** complex.

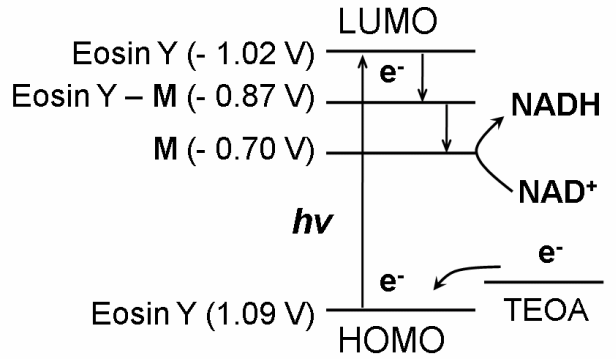

Figure S5. The suggested direction of electron flow during photosensitization of Eosin Y. The excited electron of Eosin Y cascades through the intermediate state of the Eosin Y-**M** complex. The gradient of potential and the vicinity between Eosin Y and **M** made by the Eosin Y-**M** intermediate drive the flow of electron by photosensitization. The energy level of Eosin Y and **M** is against Ag/AgCl reference electrode (+0.197 V vs. NHE). Once the electron of EY at the known HOMO (1.09 V)[3] is excited to the LUMO (-1.02 V, from Figure S5), it should cascade into **M** through the intermediate state of EY-**M** without radiation (e.g., fluorescence).

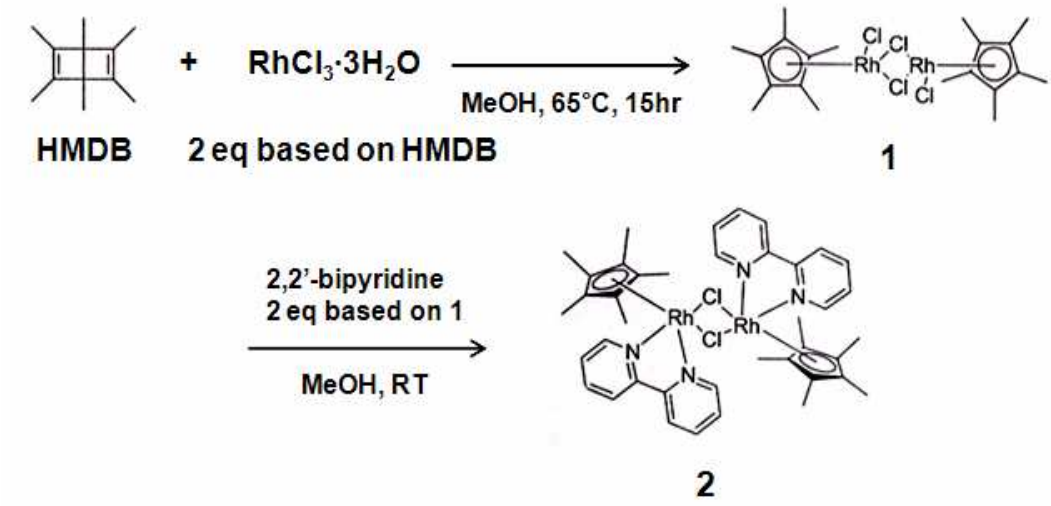

Figure S6. Synthetic procedure of organometallic compound [Cp*Rh(bpy)Cl]Cl.

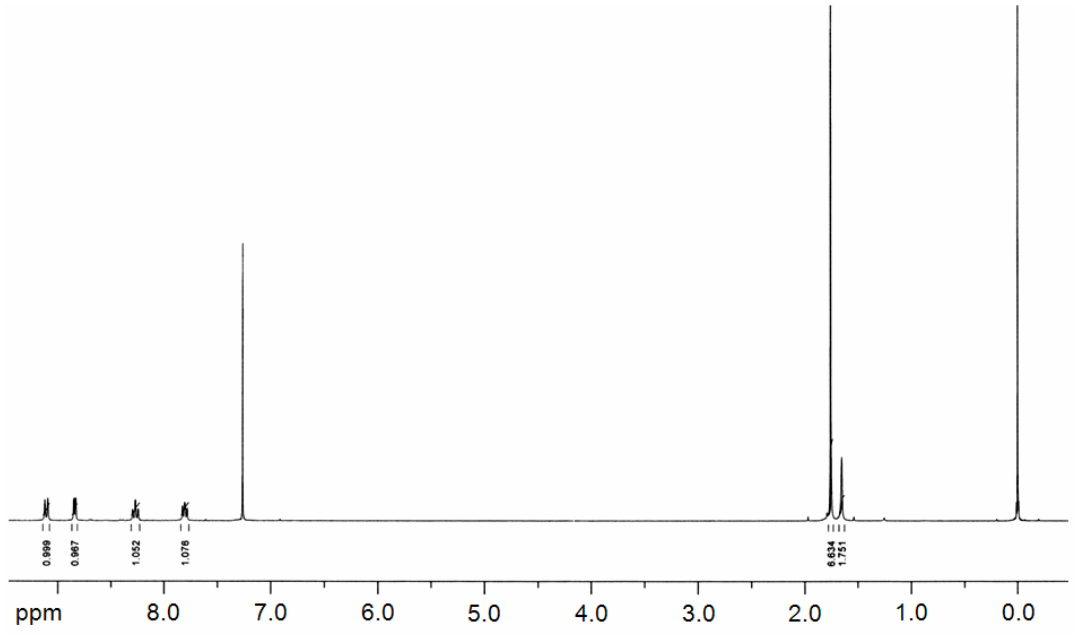

Figure S7. NMR spectrum of organometallic compound [Cp*Rh(bpy)Cl]Cl.

Detailed reaction conditions for photosensitized NADH regenerations in Figure S2

1) Eosin Y: The photoenzymatic reactor contained Eosin Y (50 μM), $[Cp^*Rh(bpy)H_2O]^{2+}$ (0.5 mM), NAD^+ (0.2 mM), substrate (α-ketoglutarate, 5 mM), ammonium sulfate (100 mM) and glutamate dehydrogenase (40 U), based on a phosphate buffer (100 mM), with TEOA (15 % *w/v*) (pH 8.0).

2) $Ru(bpy)^{3+}$:[9a] The system was consisted of an aqueous Tris buffer solution (0.1 M, pH 7.9, 3.75mL), that included $Ru(bpy)^{3+}$ (0.1 mM), 2-mercaptoethanol (20 mM), $NADP^+$ (0.88 mM), MV^{2+} (1.76 mM), NH_4^+ (0.1 M), α-oxoglutarate (0.1 M), glutamate dehydrogenase (22 U) and ferredoxin-NADP+ reductase (0.5 U).

3) PEG-chlorophyllide:[9b] The reaction mixture contained PEG-chlorophyllide conjugate (22.2 mM), ascorbate (8 mM), $NADP^+$ (3.2 mM), 2-oxoglutaric acid (8 mM), NH_4Cl (8 mM), glutamate dehydrogenase (40 U), and ferredoxin-NADP+ reductase (2.5 U) in 10 mL of 100 mM phosphate buffer (pH 7.8).

4) $W_2Fe_4Ta_2O_{17}$:[3] The photoenzymatic reactor contained $W_2Fe_4Ta_2O_{17}$ (5 mg), $[Cp^*Rh(bpy)H_2O]^{2+}$ (0.2 mM), NAD^+ (0.1 mM), $(NH_4)_2SO_4$ (5 mM), α-ketoglutarate (0.1 mM) and glutamate dehydrogenase (20 U) based on a 100 mM phosphate buffer, with EDTA (5 mM) (pH 7.0).