

Supplementary Material
for
Photocatalytic Hydrogen Evolution Using
9-Phenyl-10-methyl-acridinium Ion Derivatives as
Efficient Electron Mediators and Ru-Based
Catalysts

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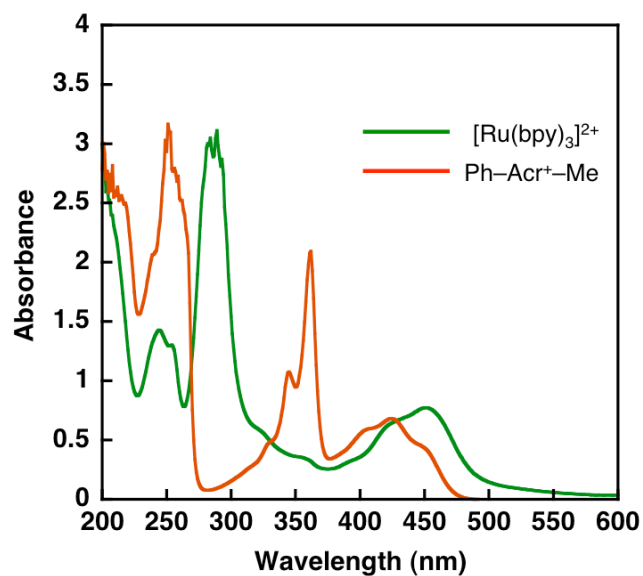


Fig. A1. UV-vis spectra of $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ (50 μM , green) and $(\text{Ph-Acr}^+-\text{Me})(\text{PF}_6)$ (100 μM , red) in MeCN.

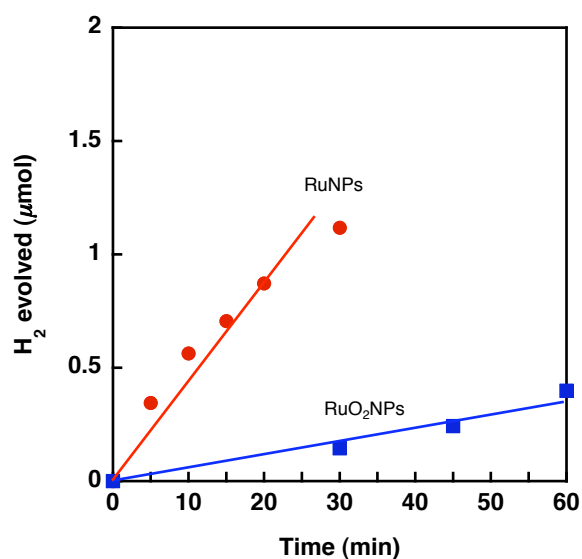


Fig. A2. Time courses of hydrogen evolution by photoirradiation ($\lambda > 420$ nm) of a mixed solution of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.20 mM), EDTA (1.0 mM), RuNPs (0.10 g L^{-1} , red circle) or RuO₂NPs (0.25 g L^{-1} , blue square) and Acr⁺-Ph-Me (0.30 mM).

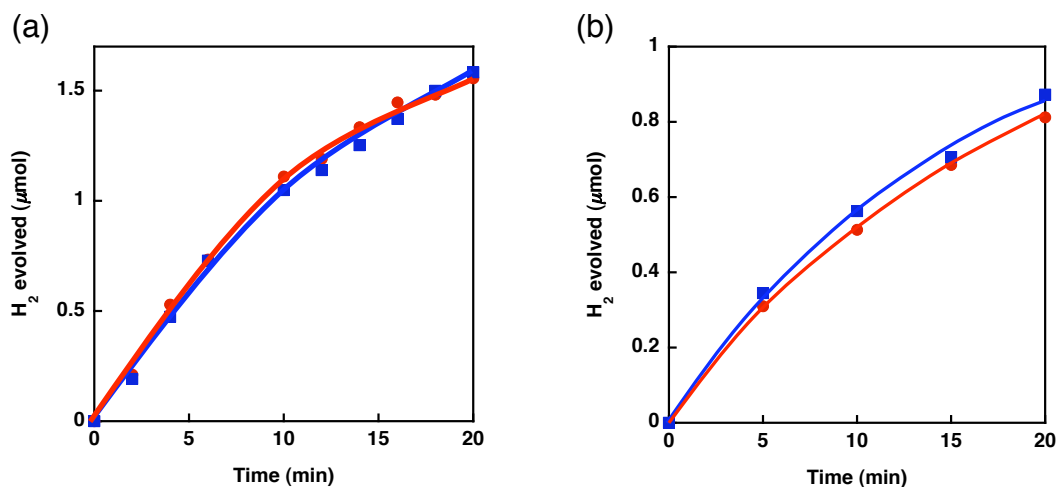


Fig. A3. (a) Time courses of hydrogen evolution by photoirradiation of a mixed solution of a phosphate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.20 mM), EDTA (1.0 mM), PtNPs (12.5 mg L^{-1}) and $\text{Acr}^+\text{-Ph}$ (0.30 mM, red circle) or $\text{Acr}^+\text{-Ph-COOH}$ (0.30 mM, blue square). (b) Time courses of hydrogen evolution by photoirradiation of a mixed solution of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.20 mM), EDTA (1.0 mM), RuNPs (0.10 g L^{-1}) and $\text{Acr}^+\text{-Ph}$ (0.30 mM, red circle) or $\text{Acr}^+\text{-Ph-COOH}$ (0.30 mM, blue square).

Calculation Procedures for the Amount of Coupled $\text{HOC}_6\text{H}_4\text{S}^-$

The ratio of $\text{HOC}_6\text{H}_4\text{S}^-$ to RuNPs: 57:43

The ratio of M (organic ligand after coupling reaction) to RuNPs: 65:35 = 79.9:43

The formula weight of $\text{HOC}_6\text{H}_4\text{S}^-$ is 126, thus, the apparent formula weight of M: $(79.9-57)/57 \times 126 = 176.6$

The formula weight of $\text{Ph-Acr}^+\text{-CH}_2\text{COOC}_6\text{H}_4\text{S}^-$ is 422. When the molar ratio of $\text{Ph-Acr}^+\text{-CH}_2\text{COOC}_6\text{H}_4\text{S}^-$ and $\text{HOC}_6\text{H}_4\text{S}^-$ was $t:(1-t)$, the apparent formula weight is $422t + 126(1-t)$

$$422t + 126(1-t) = 176 \quad t = 0.17$$

Thus, at least 17% of $\text{HOC}_6\text{H}_4\text{S}^-$ was converted to $\text{Acr}^+\text{-CH}_2\text{COOC}_6\text{H}_4\text{S}^-$, because partial removal of $\text{HOC}_6\text{H}_4\text{S}^-$ results in increases of t .

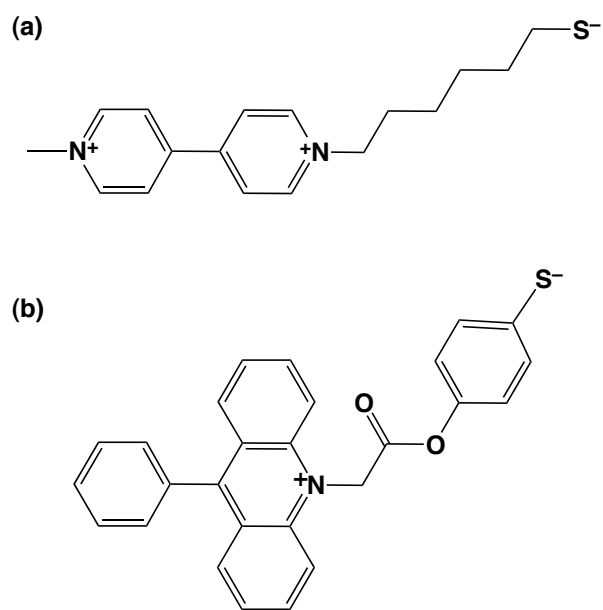


Fig. A4. Chemical structures of (a) 1-(1-hexyl-6-thiol)-1'-methyl-4,4'-bipyridinium ion and (b) $\text{Ph-Acr}^+-\text{CH}_2\text{COO-C}_6\text{H}_4\text{S}^-$.

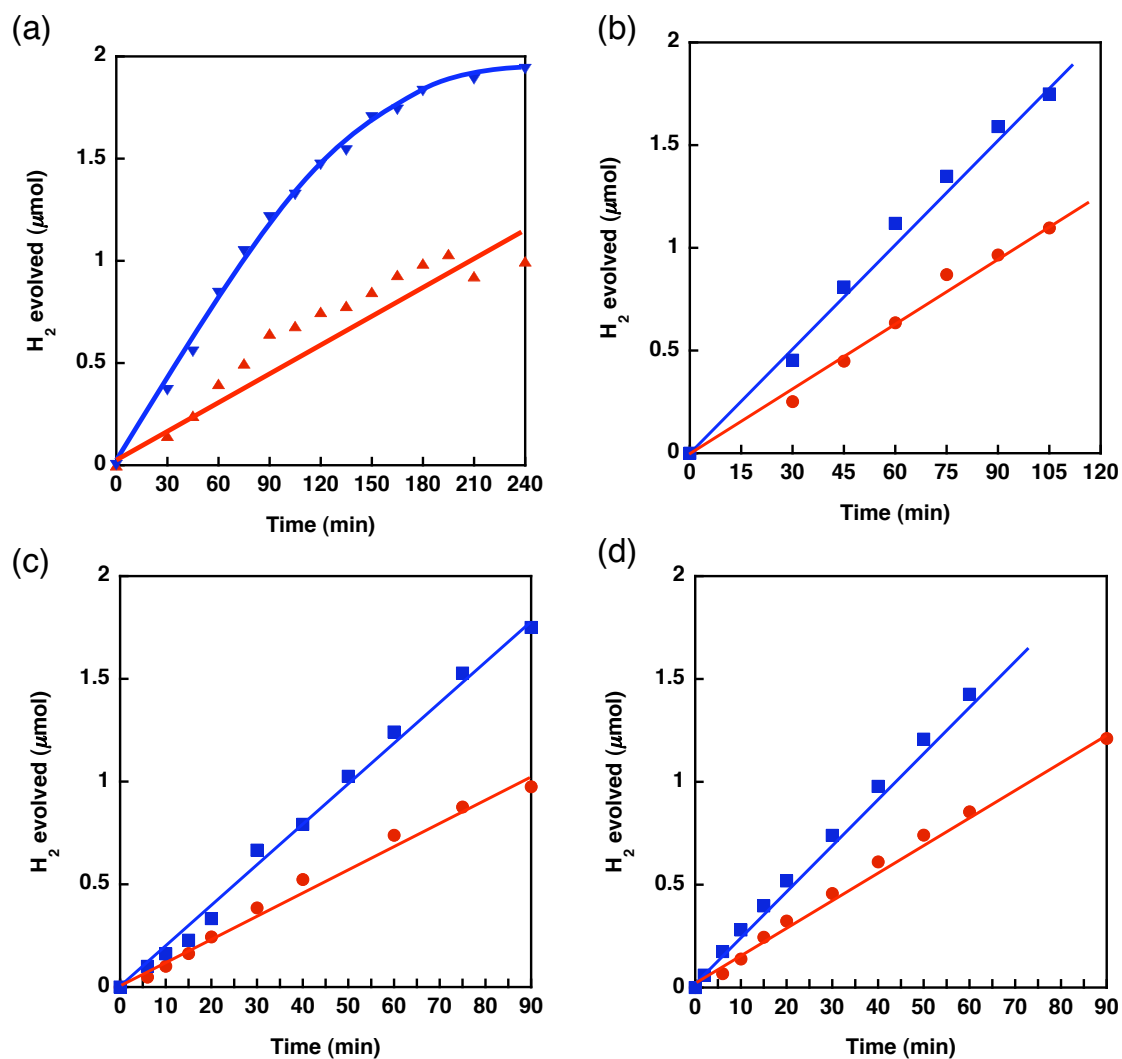


Fig. A5. Time courses of hydrogen evolution by photoirradiation ($\lambda > 420$ nm) of a mixed solution of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.20 mM), EDTA (1.0 mM), RuO_2NPs loading Pt ($0.25 \text{ g-RuO}_2 \text{ L}^{-1}$) and $\text{Acr}^+-\text{Ph}-\text{Me}$ (0.30 mM, red circle) or $\text{Acr}^+-\text{Ph}-\text{COOH}$ (0.30 mM, blue square). The loading amounts of Pt are (a) 0%, (b) 0.1%, (c) 0.5% and (d) 1.0%.