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

Yusuke Yamada, Kentaro Yano, and Shunichi Fukuzumi

A Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan
B Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea
C Correspondence author. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp
Fig. A1. UV-vis spectra of [Ru(bpy)$_3$](ClO$_4$)$_2$ (50 µM, green) and (Ph–Acr$^–$–Me)(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 [Ru(bpy)$_3$]$^{2+}$ (0.20 mM), EDTA (1.0 mM), RuNPs (0.10 g L$^{-1}$, red circle) or RuO$_2$NPs (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 [Ru(bpy)$_3$]$^{2+}$ (0.20 mM), EDTA (1.0 mM), PtNPs (12.5 mg L$^{-1}$) and Acr$^+$–Ph (0.30 mM, red circle) or Acr$^+$–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 [Ru(bpy)$_3$]$^{2+}$ (0.20 mM), EDTA (1.0 mM), RuNPs (0.10 g L$^{-1}$) and Acr$^+$–Ph (0.30 mM, red circle) or Acr$^+$–Ph–COOH (0.30 mM, blue square).

**Calculation Procedures for the Amount of Coupled HOC$_6$H$_4$S$^-$**

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

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

$$422t + 126(1-t) = 176$$

$t = 0.17$

Thus, at least 17% of HOC$_6$H$_4$S$^-$ was converted to Acr$^+$–CH$_2$COOC$_6$H$_4$S$^-$, because partial removal of HOC$_6$H$_4$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) Ph–Acr+–CH2COO-C6H4S−.
Fig. A5. Time courses of hydrogen evolution by photoirradiation (λ > 420 nm) of a mixed solution of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing [Ru(bpy)$_3$]$^{2+}$ (0.20 mM), EDTA (1.0 mM), RuO$_2$NPs loading Pt (0.25 g·RuO$_2$ L$^{-1}$) and Acr$^+$–Ph–Me (0.30 mM, red circle) or Acr$^+$–Ph–COOH (0.30 mM, blue square). The loading amounts of Pt are (a) 0%, (b) 0.1%, (c) 0.5% and (d) 1.0%.