

Electronic Supplementary Information

**Improving the Overall Performance of Photochemical H₂ Evolution
Catalyzed by the Co-NHC Complex via the Redox Tuning of Electron
Relays**

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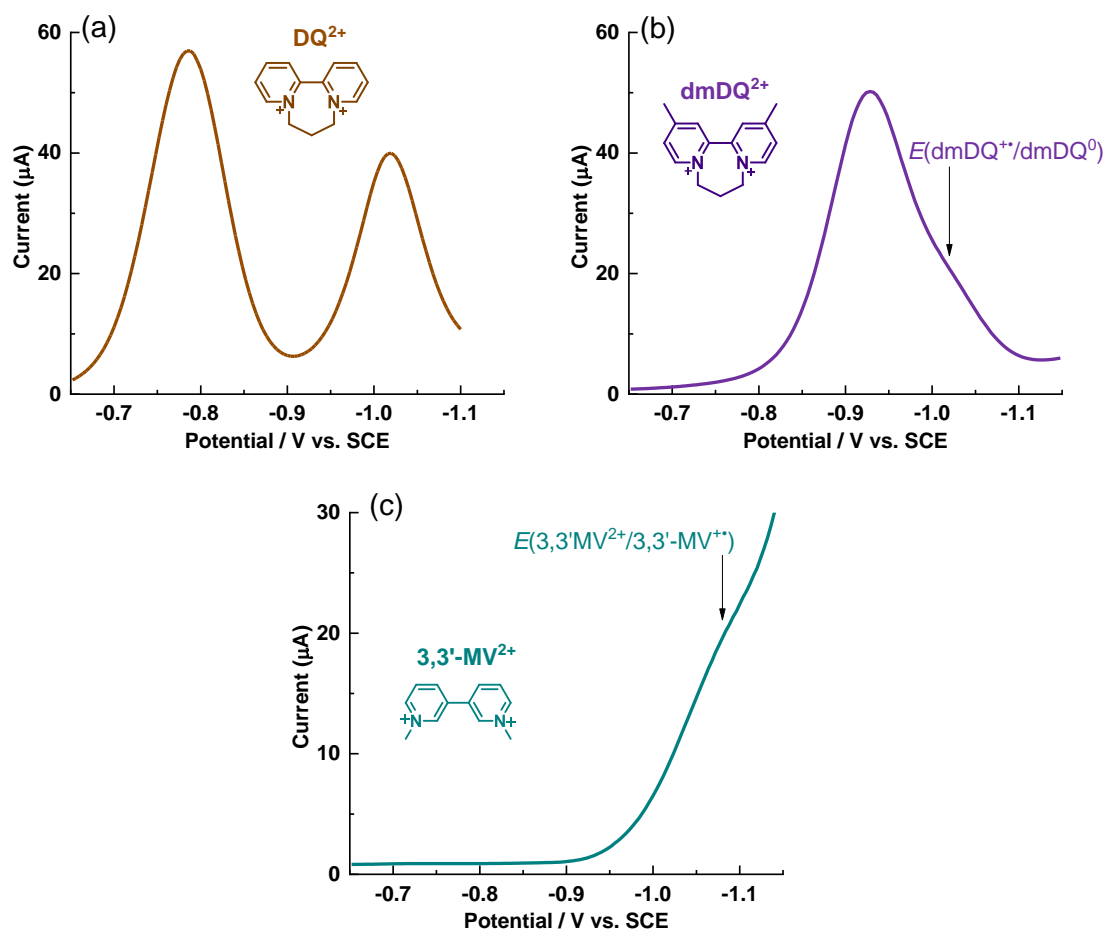


Figure S1. Square wave voltammograms of 2 mM of $\text{DQCl}_2 \cdot 1.5\text{H}_2\text{O}$ (a), $\text{dmDQCl}_2 \cdot 3\text{H}_2\text{O}$ (b), and $3,3'\text{-MVCl}_2 \cdot \text{H}_2\text{O}$ (c) in an aqueous acetate buffer solution (0.1 M, pH 5) containing KCl (0.1 M) under Ar atmosphere at room temperature. DQ^{2+} , dmDQ^{2+} and $3,3'\text{-MV}^{2+}$ denote N,N' -propylene-2,2'-bipyridinium, 4,4'-dimethyl- N,N' -propylene-2,2'-bipyridinium, and N,N' -dimethyl-3,3'-bipyridinium, respectively.

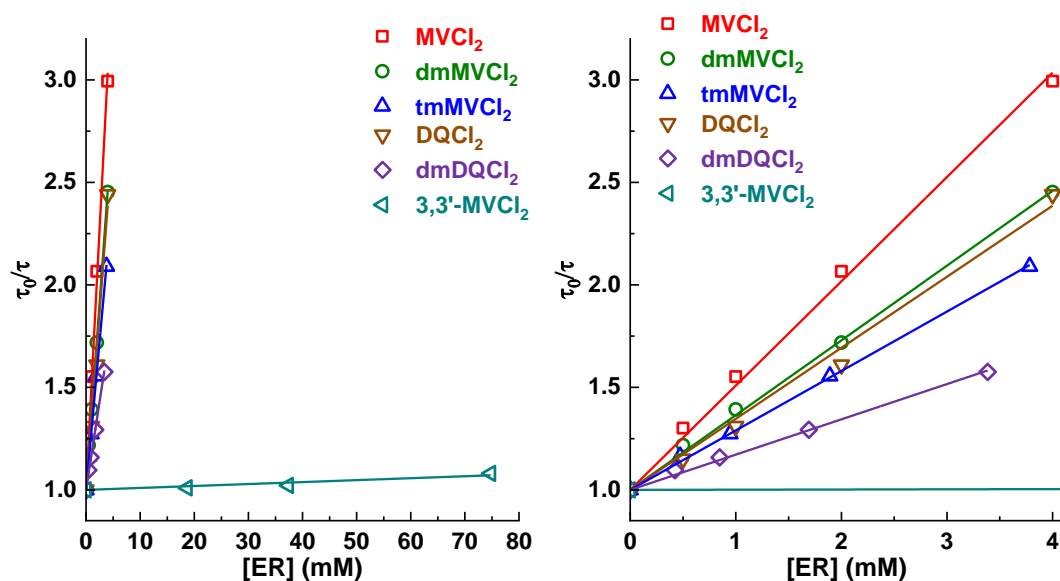


Figure S2. Stern-Volmer plots measured for the aqueous acetate buffer solutions (0.1 M, pH 5) containing [Ru(bpy)₃]²⁺·6H₂O (0.04 mM) and various concentration of electron relays (ERs) under Ar at 20 °C (left). Right Figure shows magnified plots. MV^{2+} , $dmMV^{2+}$, and $tmMV^{2+}$ denote *N,N*-dimethyl-4,4'-bipyridinium, *N,N',2,2'*-tetramethyl-4,4'-bipyridinium, and *N,N',2,2',6,6'*-hexamethyl-4,4'-bipyridinium, respectively.

Table S1. The reported values of the first reduction potentials and the quenching rate constants of ERs. These values were determined in an aqueous media. The values shown in parentheses are those determined in this study in an aqueous acetate buffer solution (0.1 M, pH 5.0).

	1st reduction potential [V vs. SCE]	Quenching rate constant of [Ru*(bpy) ₃] ²⁺ [M ⁻¹ •s ⁻¹]	Reference
MV^{2+}	-0.69 (-0.69)	9.6×10^8 (8.8×10^8)	1,2
$dmMV^{2+}$	-0.75 ^a (-0.77)	6.9×10^8 (5.9×10^8)	2
$tmMV^{2+}$	-0.88 ^a (-0.85)	4.6×10^8 (4.7×10^8)	2
DQ^{2+}	-0.79 ^a (-0.79)	5.7×10^8 (5.6×10^8)	3
$dmDQ^{2+}$	-0.94 ^a (-0.93)	4.0×10^8 (2.8×10^8)	3
$3,3'-MV^{2+}$	-1.08 ^b (-1.08)	1.0×10^{10} (1.5×10^6)	4

^aValues are reported as V vs. NHE, and converted into V vs. SCE using following equation; 0 V vs NHE = -0.24 V vs SCE. ^bReduction potential was measured in acetonitrile.

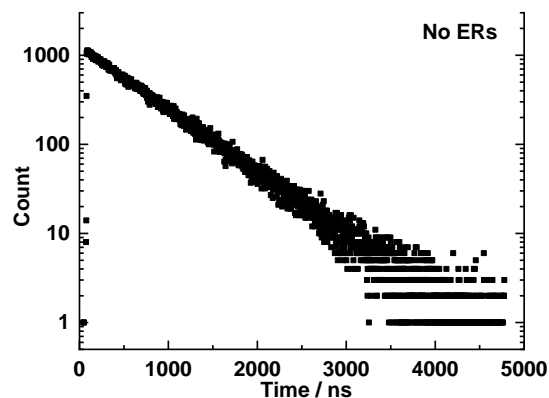


Figure S3. Emission decay profile of an aqueous acetate buffer solution (0.1 M, pH 5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

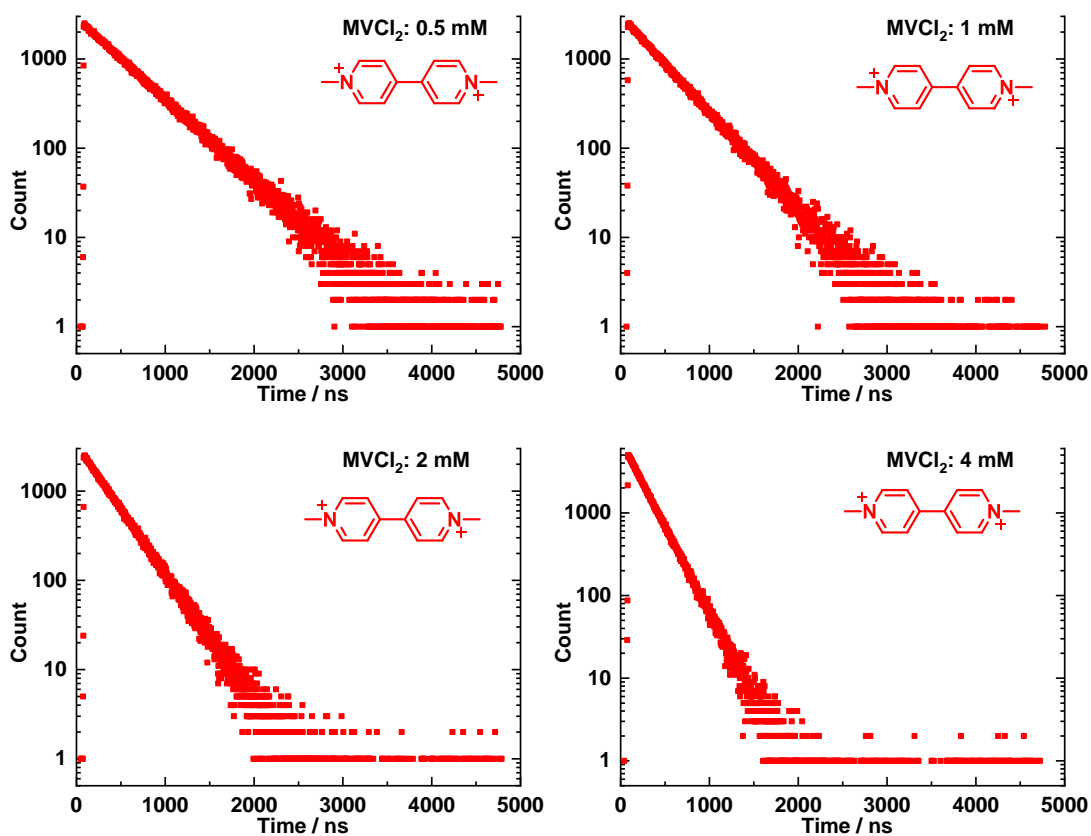


Figure S4. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) and various concentrations of $\text{MVCl}_2 \cdot 3\text{H}_2\text{O}$ (0.5, 1, 2 and 4 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

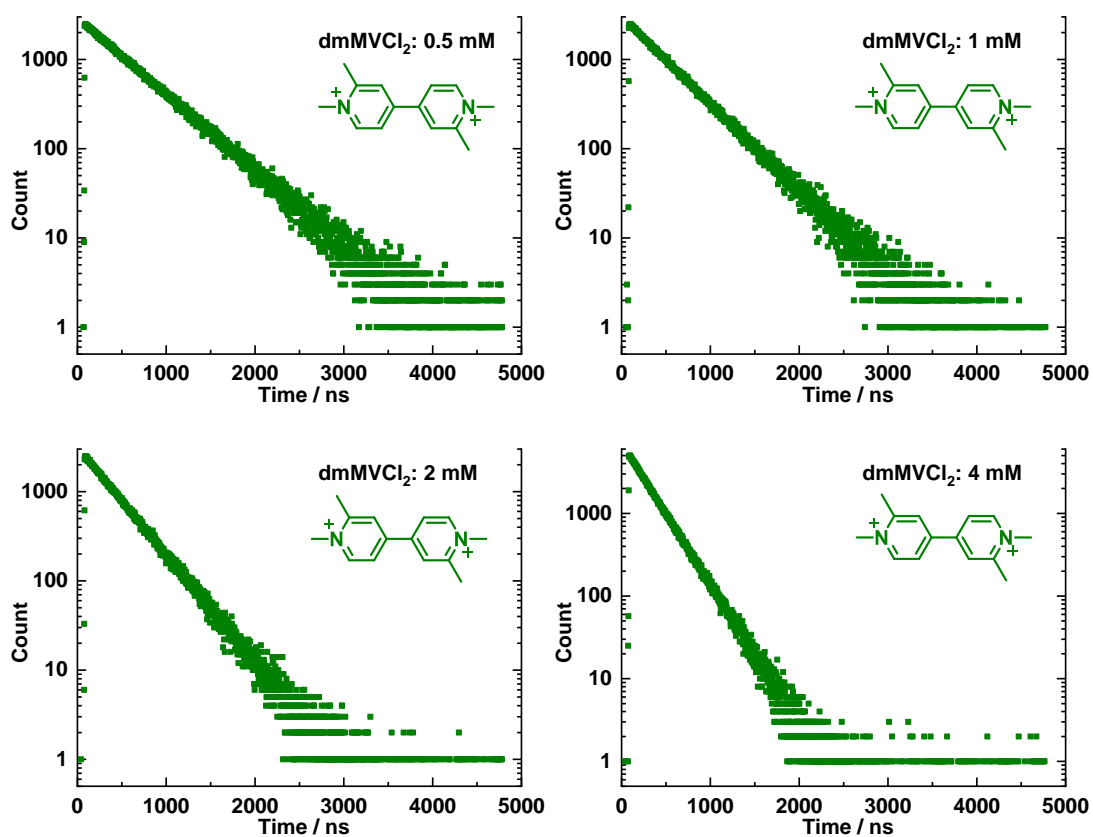


Figure S5. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) and various concentrations of $\text{dmMVCl}_2 \cdot 1.5\text{H}_2\text{O}$ (0.5, 1, 2 and 4 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

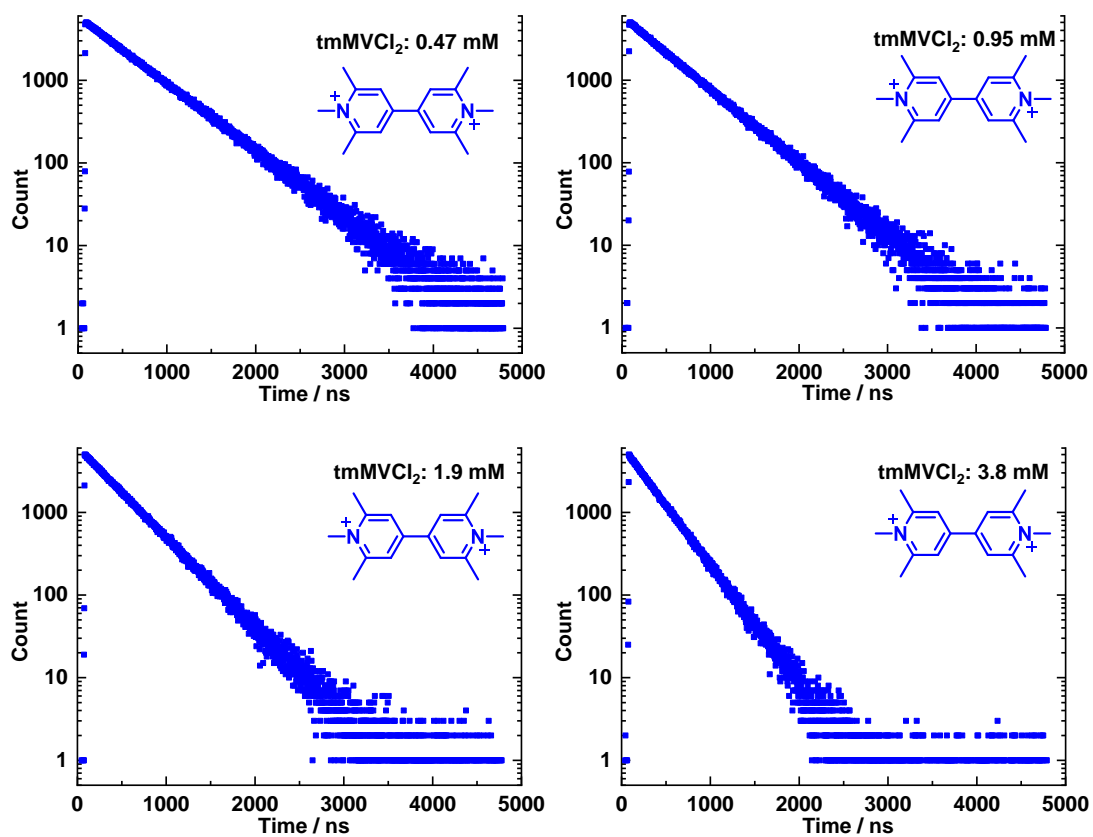


Figure S6. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing [Ru(bpy)₃]Cl₂·6H₂O (0.04 mM) and various concentrations of tmMVCl₂·H₂O (0.47, 0.95, 1.9 and 3.8 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

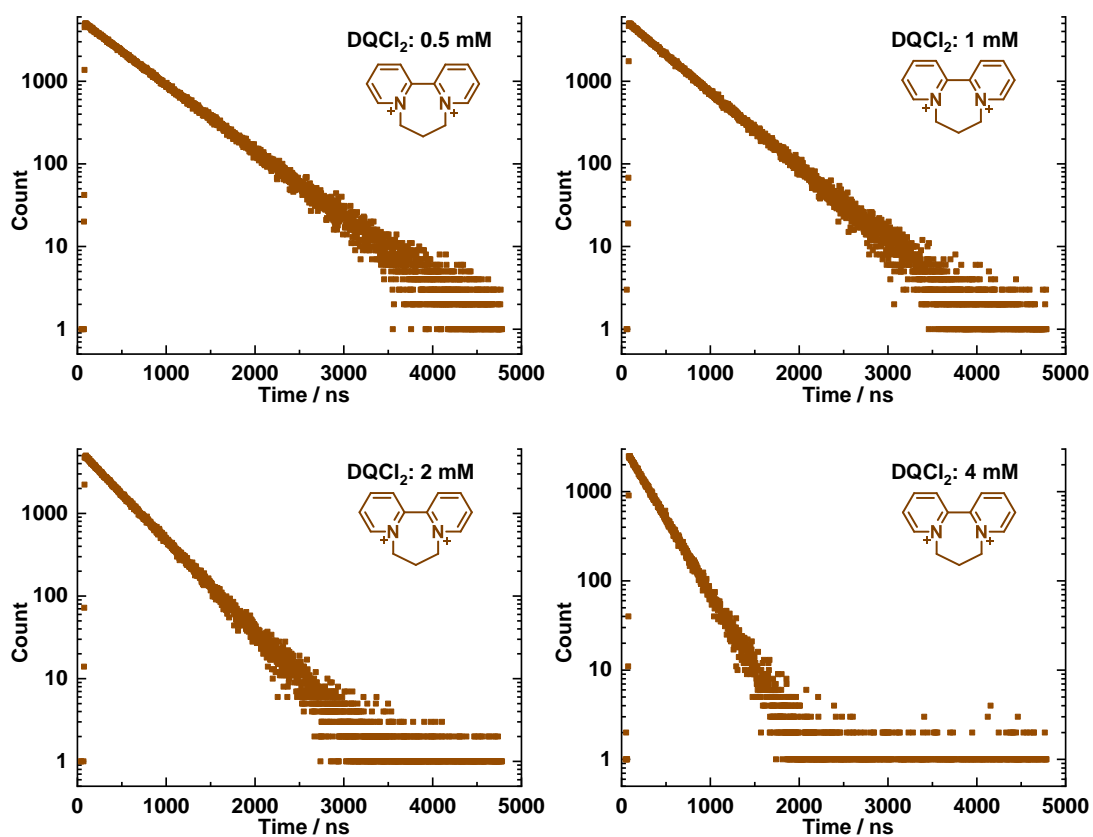


Figure S7. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) and various concentrations of $\text{DQCl}_2 \cdot 1.5\text{H}_2\text{O}$ (0.5, 1, 2 and 4 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

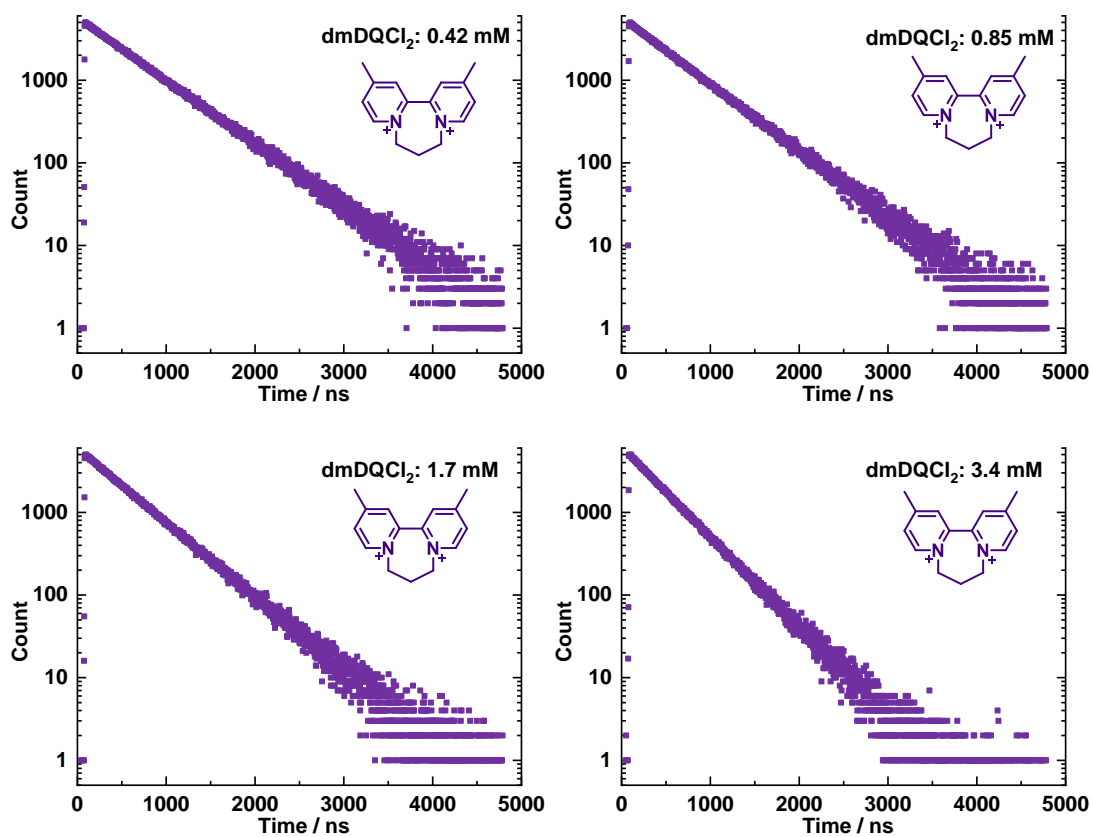


Figure S8. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) and various concentrations of $\text{dmDQCl}_2 \cdot 3\text{H}_2\text{O}$ (0.42, 0.85, 1.7 and 3.4 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

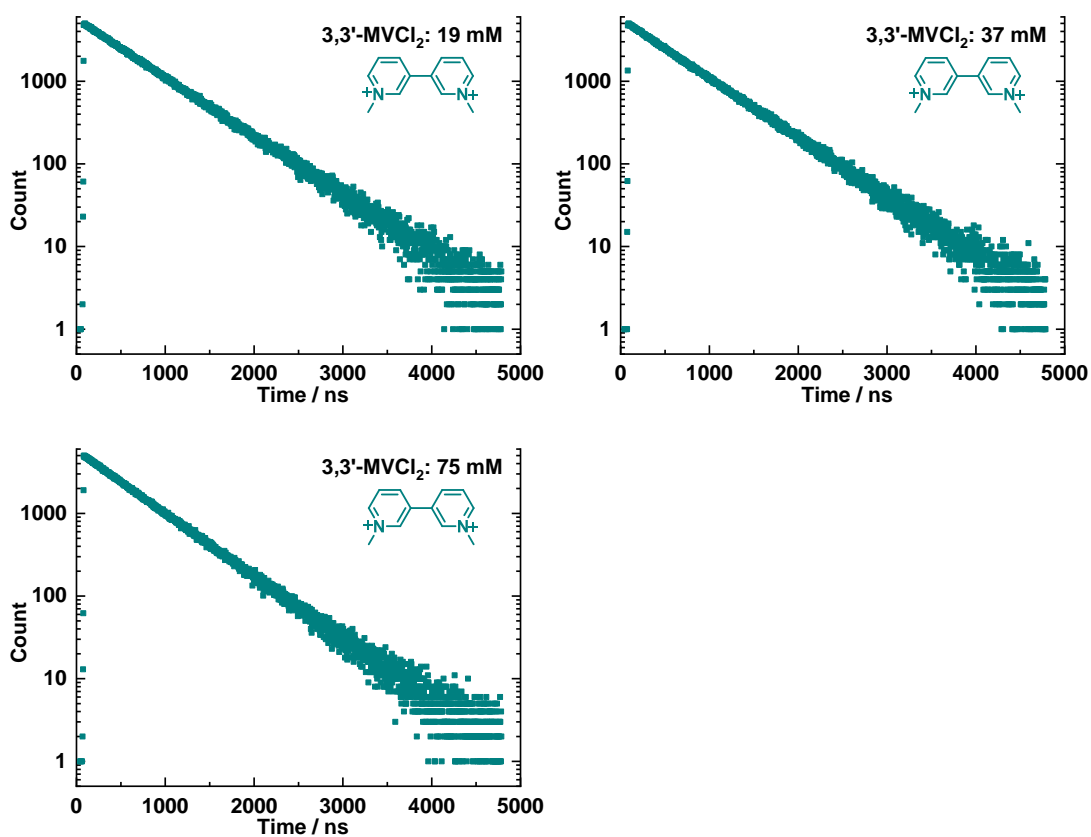


Figure S9. Emission decay profiles of aqueous acetate buffer solutions (0.1 M, pH 5) containing [Ru(bpy)₃]Cl₂·6H₂O (0.04 mM) and various concentrations of 3,3'-MVCl₂·H₂O (19, 37 and 75 mM) under Ar atmosphere at 20 °C. The excitation wavelength was 472 nm, and the emission was monitored at 600 nm.

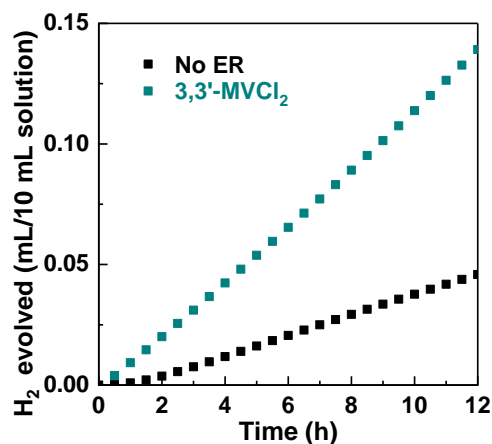


Figure S10. Photochemical H₂ production from an aqueous acetate buffer solution (0.1 M; pH 5.0; 10 mL) containing EDTA (ethylenediaminetetraacetic acid disodium salt; 30 mM), [Ru(bpy)₃]Cl₂·6H₂O (0.04 mM), and Co-NHC-1 (0.1 mM) in the presence and absence of 3,3'-MVCl₂·H₂O (2 mM), under Ar atmosphere at 20 °C. Due to the inevitable difference between the Xe lamp used in this measurement and that used for Figure 2 in MS, the values of the initial rate of HER cannot be compared with those shown in Figure 2 in MS. The other experimental conditions are same to those described in Figure 2 in MS.

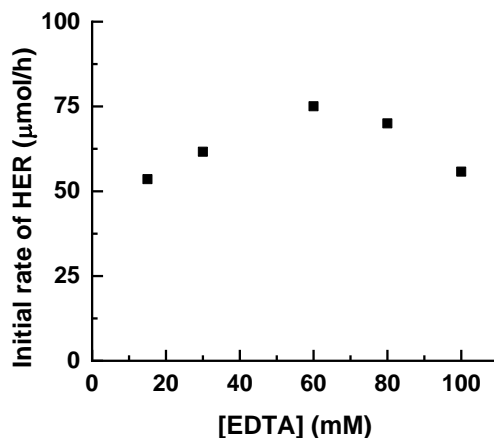


Figure S11. Dependence of the initial rate of HER on the EDTA concentration. Photolysis was carried out using the photolysis solution containing [Ru(bpy)₃]Cl₂·6H₂O (0.04 mM), Co-NHC-1 (0.1 mM), tmMVCl₂·H₂O (2 mM), and varying concentration of EDTA (disodium salt). The initial rate of HER is calculated by using the amount of H₂ evolved at 10 min of photolysis. Due to the inevitable difference between the Xe lamp used in this measurement and that used for Figure 2 in MS, the values of the initial rate of HER cannot be compared with those shown in Figure 2 in MS. The other experimental conditions are same to those described in Figure 2 in MS.

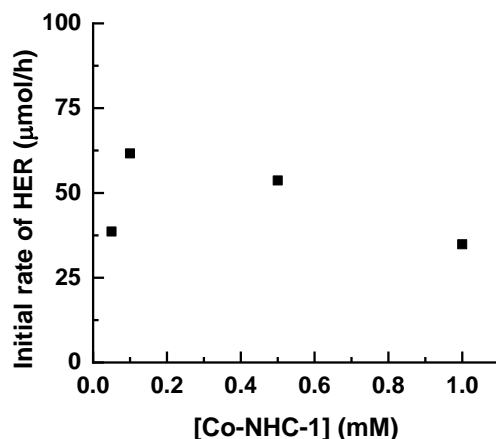


Figure S12. Dependence of the initial rate of HER on the **Co-NHC-1** concentration. Photolysis was carried out using the photolysis solution containing EDTA (30 mM; disodium salt), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM), $\text{tmMVC1}_2 \cdot \text{H}_2\text{O}$ (2 mM), and varying concentration of **Co-NHC-1**. The initial rate of HER is calculated by using the amount of H_2 evolved at 10 min of photolysis. Due to the inevitable difference between the Xe lamp used in this measurement and that used for Figure 2 in MS, the values of the initial rate of HER cannot be compared with those shown in Figure 2 in MS. The other experimental conditions are same to those described in Figure 2 in MS.

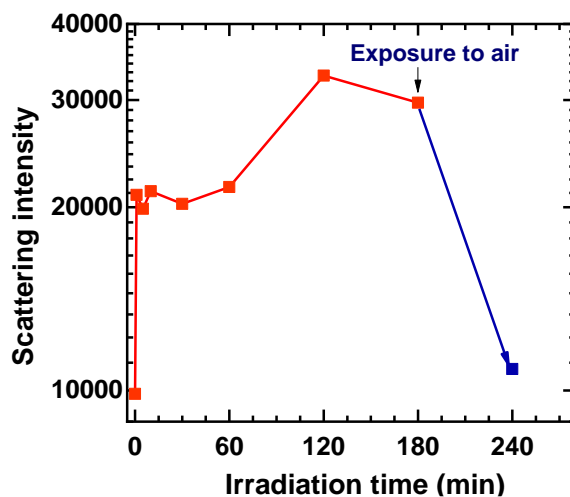


Figure S13. Changes in the light scattering intensity of an aqueous acetate buffer solution (0.1 M, pH 5) containing EDTA (30 mM; disodium salt), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM) and $\text{tmMVC1}_2 \cdot \text{H}_2\text{O}$ (2 mM) during the visible light irradiation ($\lambda > 400 \text{ nm}$) under Ar atmosphere at 20 °C. After 180 min of light irradiation, the resulting solution was exposed to air and left for 60 min.

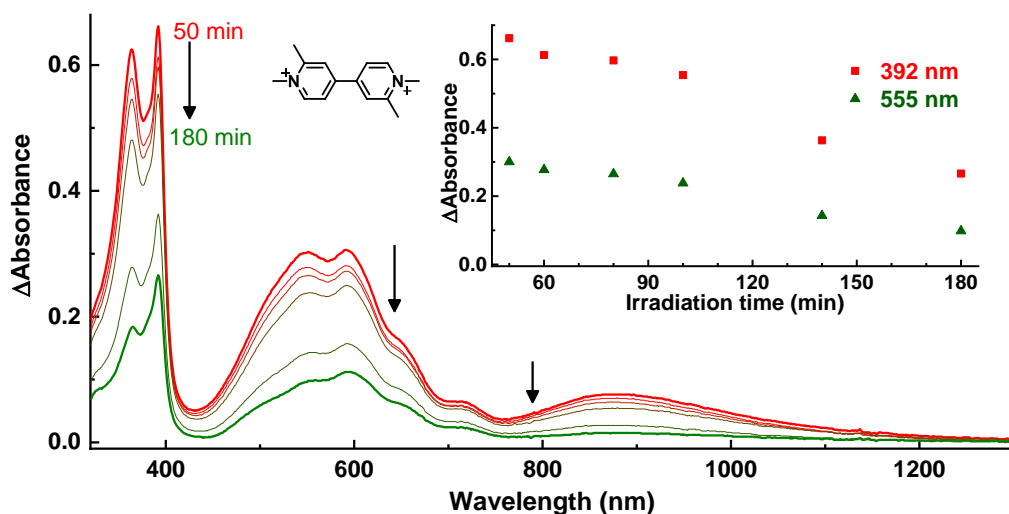


Figure S14. Spectral changes of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing EDTA (30 mM; disodium salt), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM), and $\text{dmMVCl}_2 \cdot 1.5\text{H}_2\text{O}$ (2 mM) during 180 min of visible light irradiation ($\lambda > 400$ nm) using a 300 W Xe lamp under Ar atmosphere at 20 °C. Inset shows the time courses of absorbance changes at 392 and 555 nm. The spectral changes during the initial 50 min are shown in Figure 5 in the main MS.

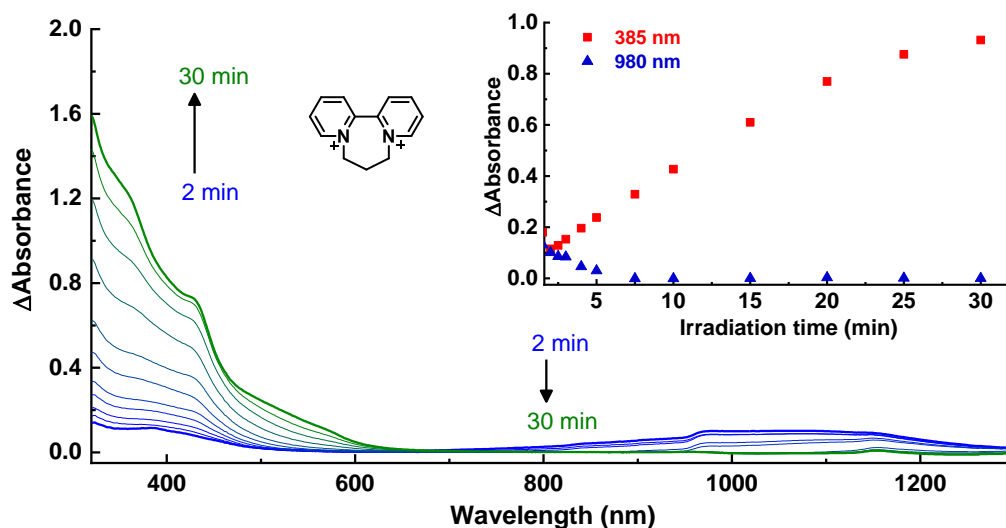


Figure S15. Spectral changes of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing EDTA (30 mM; disodium salt), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM), and $\text{DQCl}_2 \cdot 1.5\text{H}_2\text{O}$ (2 mM) during 30 min of visible light irradiation ($\lambda > 400$ nm) using a 300 W Xe lamp under Ar atmosphere at 20 °C. Inset shows the time courses of absorbance changes at 385 and 980 nm. The spectral changes during the initial 2 min are shown in Figure 6 in the main MS.

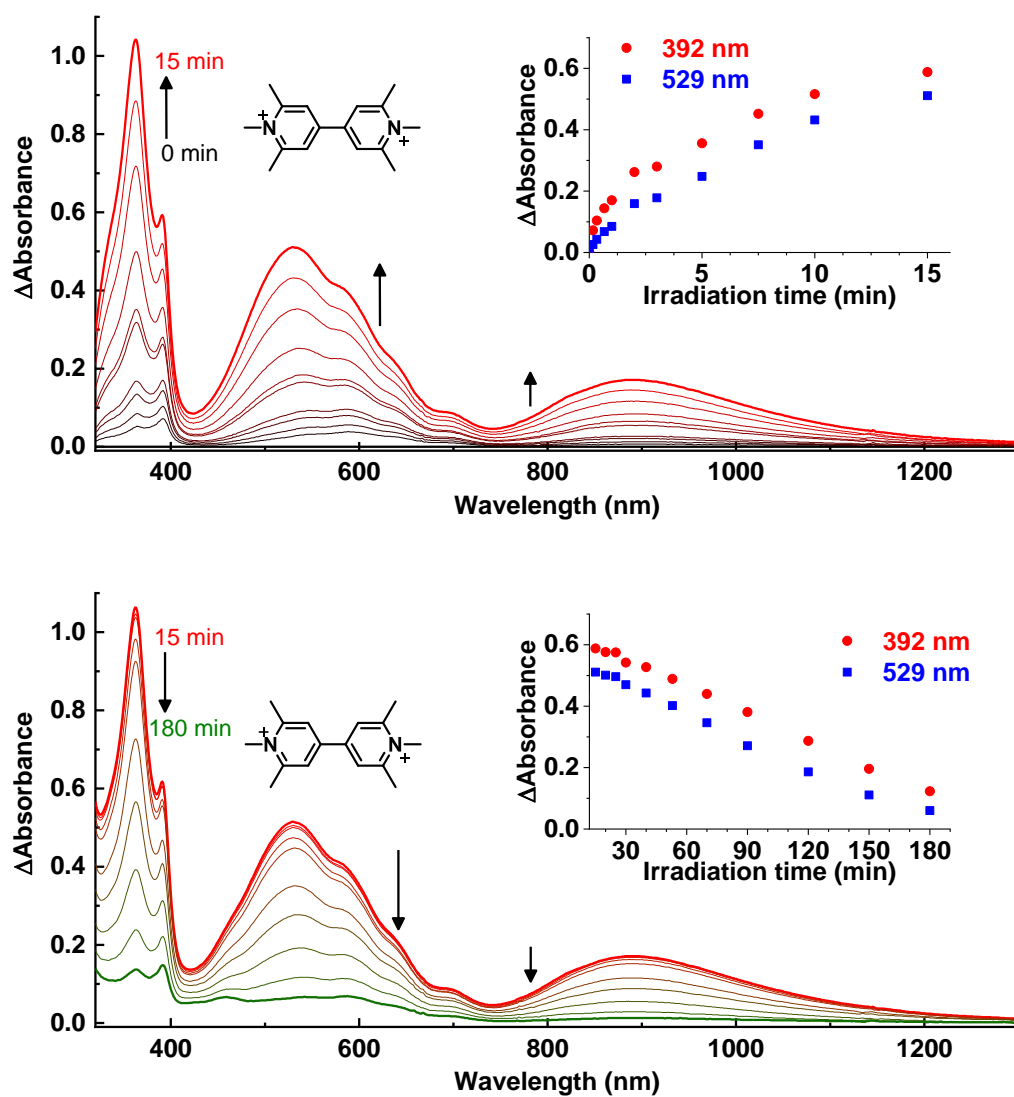


Figure S16. Spectral changes of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing EDTA (30 mM; disodium salt), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mM), and $\text{tmMVCl}_2 \cdot \text{H}_2\text{O}$ (2 mM) during 180 min of visible light irradiation using a 300 W Xe lamp under Ar atmosphere at 20 °C. Inset shows the time courses of absorbance changes at 392 and 529 nm. Top Figure shows spectral changes from 0 to 15 min, and bottom Figure shows those from 15 to 180 min.

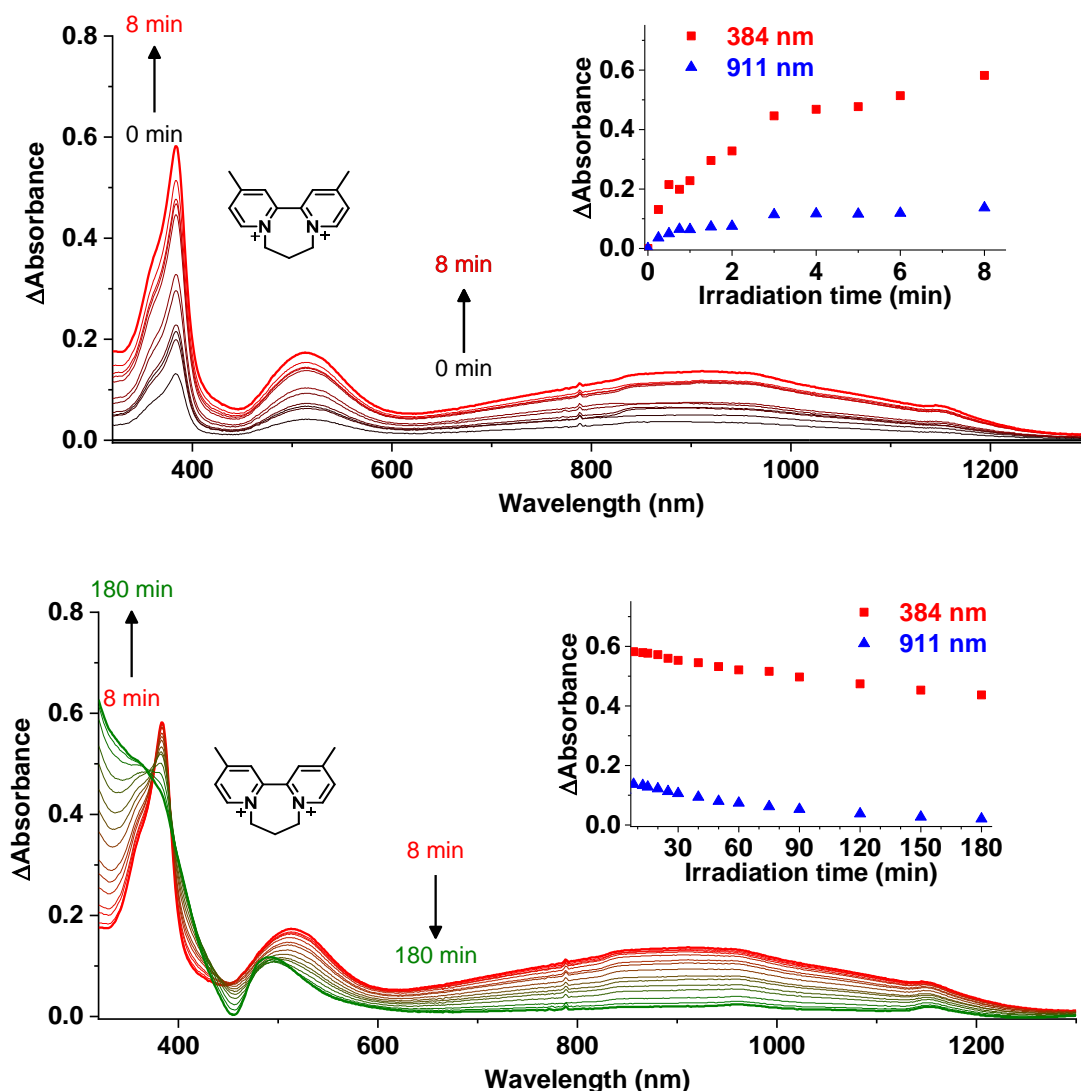


Figure S17. Spectral changes of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing EDTA (30 mM; disodium salt), [Ru(bpy)₃]Cl₂·6H₂O (0.04 mM), and **dmDQ**Cl₂·3H₂O (2 mM) during 180 min of visible light irradiation using a 300 W Xe lamp under Ar atmosphere at 20 °C. Inset shows the time courses of absorbance changes at 384 and 911 nm. Top Figure shows spectral changes from 0 to 8 min, and bottom Figure shows those from 8 to 180 min.

References

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