Electronic Supplementary Material (ESI) for Chemical Science.

Highly Efficient, Selective, and Durable Photocatalytic System for CO_2 Reduction to Formic Acid

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Supporting Information

Light Irradiation Condition (LIC):

LIC1 for determining Φ□ The quantum yield measurements were performed in an 11 mL quartz cubic cell (light pass length: 1 cm) containing a 4 mL DMF–TEOA (4:1 v/v) solution a photocatalyst and a sacrificial electron donor (0.1 M), following purging with CO_2 for 20 min. For evaluating the number of photons absorbed by the photocatalyst, monochromic light is required. The quantum yields were measured in the two different condition of [**Ru_2-Ru(CO)**] = 0.15 mM and 0.025 mM.

- When [**Ru_2-Ru(CO)**] was 0.15 mM, the absorbance of the reaction solution at the wavelength of irradiation should be sufficiently high, at least 2 where 99 % of the irradiated photons is absorbed by the photocatalyst. We used 480-nm monochromic light obtained using a 500-W Xe lamp with a band-pass filter (FWHM = 10 nm) and a 5-cm long $CuSO_4$ solution (250 g/L) filter. The incident light flux was completely absorbed by the photosensitizer unit because the absorbance of the reaction solutions was larger than 3 at 480 nm.
- Using 0.025 mM of **Ru_2-Ru(CO)**, the quantum yields were obtained using a Shimadzu photoreaction quantum yield evaluation system QYM–01. The number of absorbed photons could be calculated from the change in absorbance at the wavelength of irradiation. A 300 W Xe lamp equipped with a 480-nm (FWHM: 10 nm) band-pass filter was employed for the irradiation.

The light intensity was 5.0×10^{-9} einstein·s^{-1}, which was controlled using ND filters. The solution was vigorously mixed during the irradiation. During irradiation the temperatures of the solutions were maintained at 25 °C using an IWAKI constant temperature system CTS-134A.

The photon flux determined the rates of the photocatalytic reactions, i.e., the ordinary light source, even 500-W or 300-W Xe lamp, cannot supply enough photon flux for determining maximum TOF values. For obtaining more exact values of TON and TOF, we reduced the concentrations of the photocatalysts in the reaction solutions and used different light sources as follows.

LIC2 for determining TON: Photocatalytic reactions were performed in 11 mL Pyrex glass tubes (i.d. = 8 mm) containing a 4 mL of DMF–TEOA (4:1 v/v) solution a photocatalyst (0.025 mM) and a sacrificial electron donor (0.1 M), following purging with CO_2 for 20 min. λ_{ex} > 500-nm light was obtained using a 500-W high pressure mercury lamp equipped with a uranyl glass and a K_2CrO_4 (30 % w/w, d = 1 cm) aqueous solution filter, which supplied stronger light flux than that used in **LIC1**. The TONs were determined after 25-h or 20-h irradiation, and calculated as the produced amount of formic acid divided by the amount of supramolecule added. Using a merry-go-round irradiation apparatus, we could irradiate up to

8 samples simultaneously with the same light-intensity. During irradiation, the temperature of the solutions was maintained at 25 °C using a constant temperature system EYELA CTP-1000.

LIC3 for determining TOF: A 4-mL solution in an 11 mL quartz cubic cell (light pass length: 1 cm) was irradiated with light at $\lambda_{ex} > 420$ nm using a high-pressure mercury lamp with a 5-cm long $CuSO_4$ solution (250 g/L) filter and a cutoff filter ($\lambda > 420$ nm). This visible-light source could irradiate the reaction solution with the highest intensity in our laboratory.

Derivation of the differential equations:

According to Scheme 1, the time courses of the concentrations of each species are summarized as eqs. 1-5.

$$\mathrm{d}[{}^3(^*\mathbf{Ru})]/\mathrm{dt} = -\,(k_\mathrm{d} + k_\mathrm{q}[\mathrm{BI(OH)H}])[{}^3(^*\mathbf{Ru})] \tag{1}$$

$$\mathrm{d}[(\mathbf{Ru}^{-}\cdots\mathrm{BI(OH)H}^{\cdot+})]/\mathrm{dt} = -\,(k_\mathrm{esc} + k_\mathrm{rec1})[(\mathbf{Ru}^{-}\cdots\mathrm{BI(OH)H}^{\cdot+})] + k_\mathrm{q}[\mathrm{BI(OH)H}][{}^3(^*\mathbf{Ru})] \tag{2}$$

$$\mathrm{d}[\mathrm{BI(OH)H}^{\cdot+}]/\mathrm{dt} = k_\mathrm{esc}[(\mathbf{Ru}^{-}\cdots\mathrm{BI(OH)H}^{\cdot+})] - (k_\mathrm{dp}[\mathrm{B}] + k_\mathrm{rec2}[\mathbf{Ru}^{-}])[\mathrm{BI(OH)H}^{\cdot+}] \tag{3}$$

$$\mathrm{d}[\mathrm{BI(OH)}\cdot]/\mathrm{dt} = k_\mathrm{dp}[\mathrm{B}][\mathrm{BI(OH)H}^{\cdot+}] - k_\mathrm{et}[\mathbf{Ru}][\mathrm{BI(OH)}\cdot] \tag{4}$$

$$\mathrm{d}[\mathbf{Ru}^{-}]/\mathrm{dt} = k_\mathrm{esc}[(\mathbf{Ru}^{-}\cdots\mathrm{BI(OH)H}^{\cdot+})] + k_\mathrm{et}[\mathbf{Ru}][\mathrm{BI(OH)}\cdot] - k_\mathrm{rec2}[\mathbf{Ru}^{-}][\mathrm{BI(OH)H}^{\cdot+}] \tag{5}$$

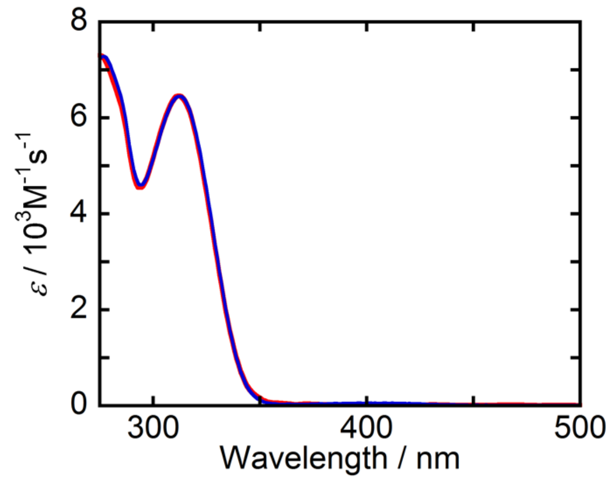

Figure S1. UV–vis absorption spectra of BI(OH)H in DMF–TEOA (4:1 v/v, red line) and in DMF (blue line).

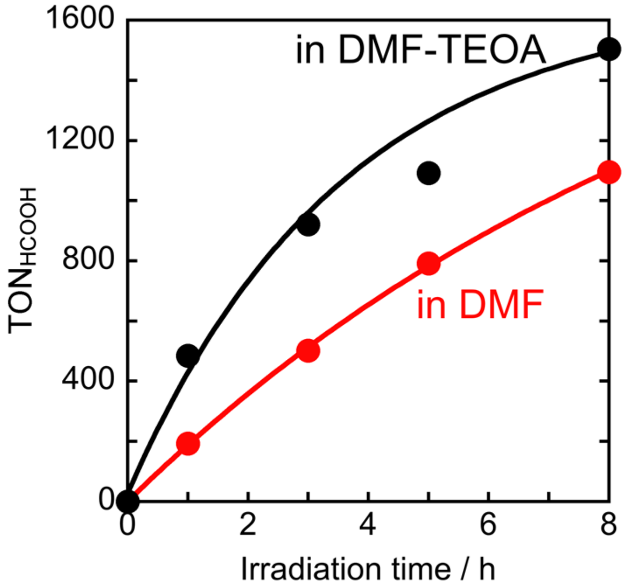

Figure S2. Photocatalytic formation of formic acid as a function of irradiation time in DMF (●) or in DMF–TEOA (4:1 v/v, ●): a CO_2 saturated DMF–TEOA (4:1 v/v, 2 mL) solution containing **Ru_2-Ru(CO)** (0.025 mM) and BI(OH)H (0.1 M) was irradiated using $\lambda_{ex} > 500$-nm light (**LIC2**).