

Electronic Supplementary Information

Development of a panchromatic photosensitizer
and its application to photocatalytic CO₂ reduction

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Table S1. DFT-calculated characteristics of frontier molecular orbitals of **Os** in ground state.

	E / eV	contributes		
		mbip	Os	mtpy
LUMO+3	-2.62	52	4	43
LUMO+2	-2.70	46	0	54
LUMO+1	-2.79	0	11	89
LUMO	-2.83	87	11	2
HOMO	-5.71	28	57	15
HOMO-1	-6.05	11	63	26
HOMO-2	-6.08	29	61	10

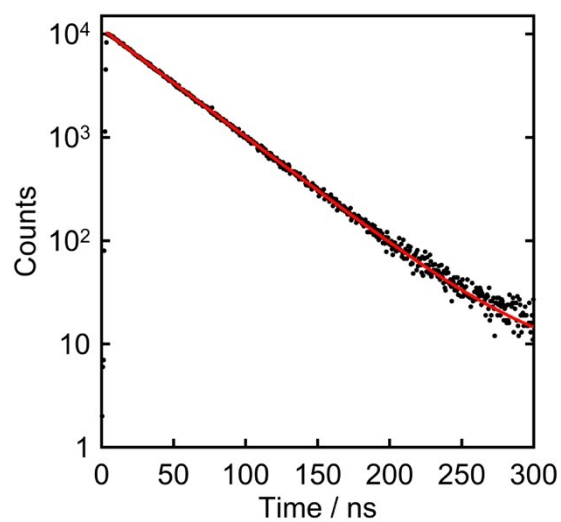


Figure S1. Single-photon counting plots of transient emission at 795 nm from DMA solution of **Os** (●) and its single-exponential fitting (red line). LED pulse (456 nm; pulse duration: 1.3 ns) was used for the excitation light source.

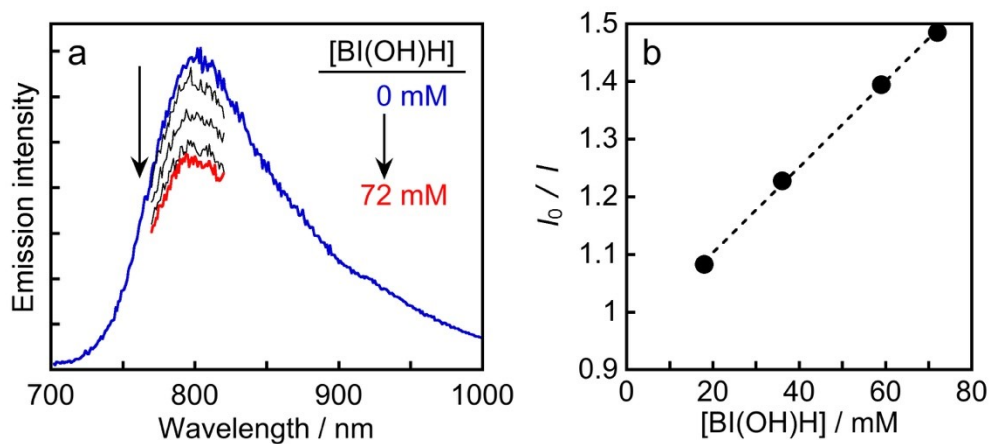


Figure S2. (a) Emission spectra of CO₂-saturated DMA solutions containing **Os** and BI(OH)H at five different concentrations. (b) Stern-Volmer plot of emission intensity from **Os** against BI(OH)H concentration. Excitation wavelength was 550 nm.

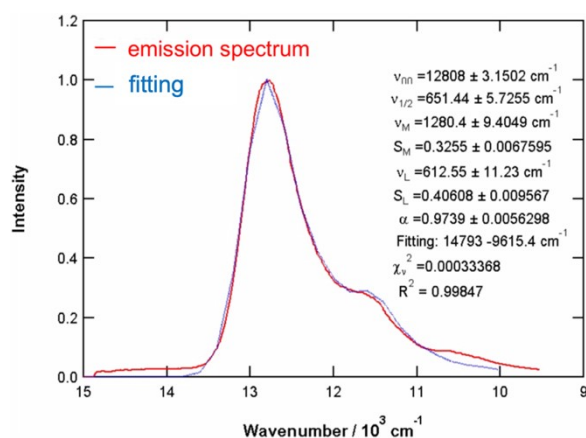


Figure S3. Emission spectrum of **Os** measured in frozen DMA by liquid nitrogen (red line) and its Franck-Condon fitting (blue line).

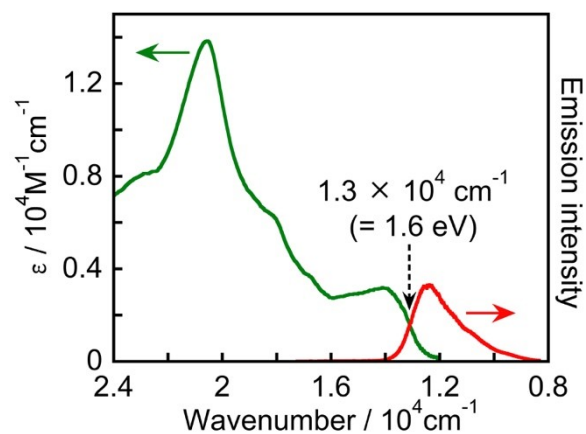


Figure S4. Normalized absorption (green line) and emission (red line) spectra of **Os** in DMA.

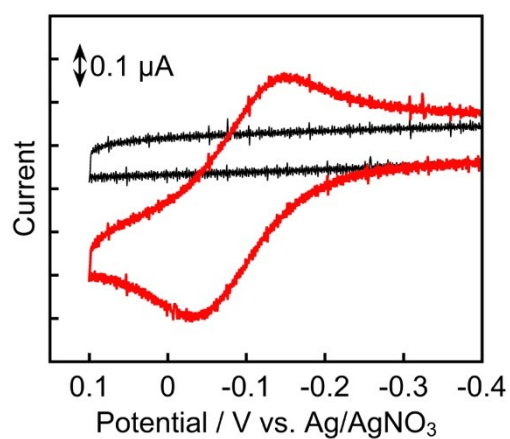


Figure S5. Cyclic voltammogram of BI(OH)H (5 mM) (red line) in an Ar-saturated DMA solution containing Et_4NBF_4 (0.1 M) as a supporting electrolyte with a Ag/AgNO_3 (10 mM) reference electrode and micro glassy-carbon working electrode ($\phi = 33 \mu\text{m}$). Scan rate was $200 \text{ V}\cdot\text{s}^{-1}$. Black line shows the background current.

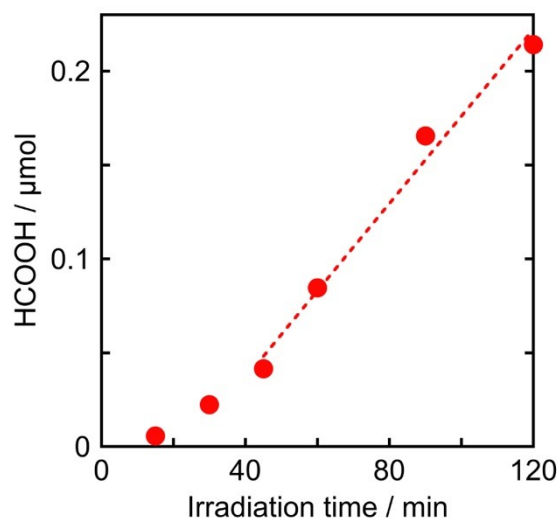


Figure S6. Photocatalytic formation of HCOOH: CO₂-saturated DMA solutions (3.5 mL) containing **Os** (50 μM), **Ru(CO)** (50 μM) and BI(OH)H (0.2 M) were irradiated at 480-nm light. Light intensity was 7.5×10^{-8} einstein·s⁻¹.

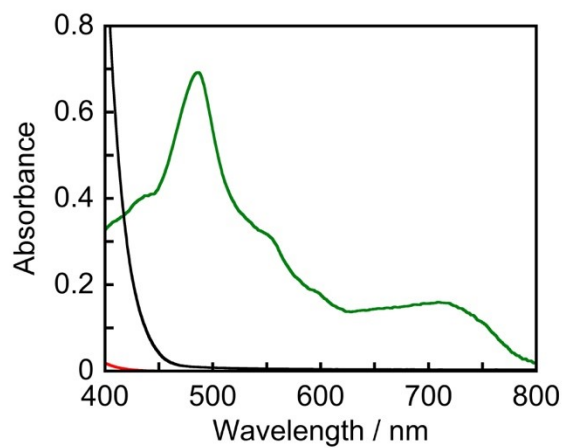


Figure S7. Visible absorption spectra of **Os** (50 μM, green line), **Ru(CO)** (50 μM, red line) and BI(OH)H (0.2 M, black line) in DMA. Light-pass length was 10 mm.