Supplementary Information

Bifunctional conjugated polymer photocatalysts for visible light water oxidation and CO_2 reduction: Function- and site-selective hybridisation of Ru(II) complex catalysts

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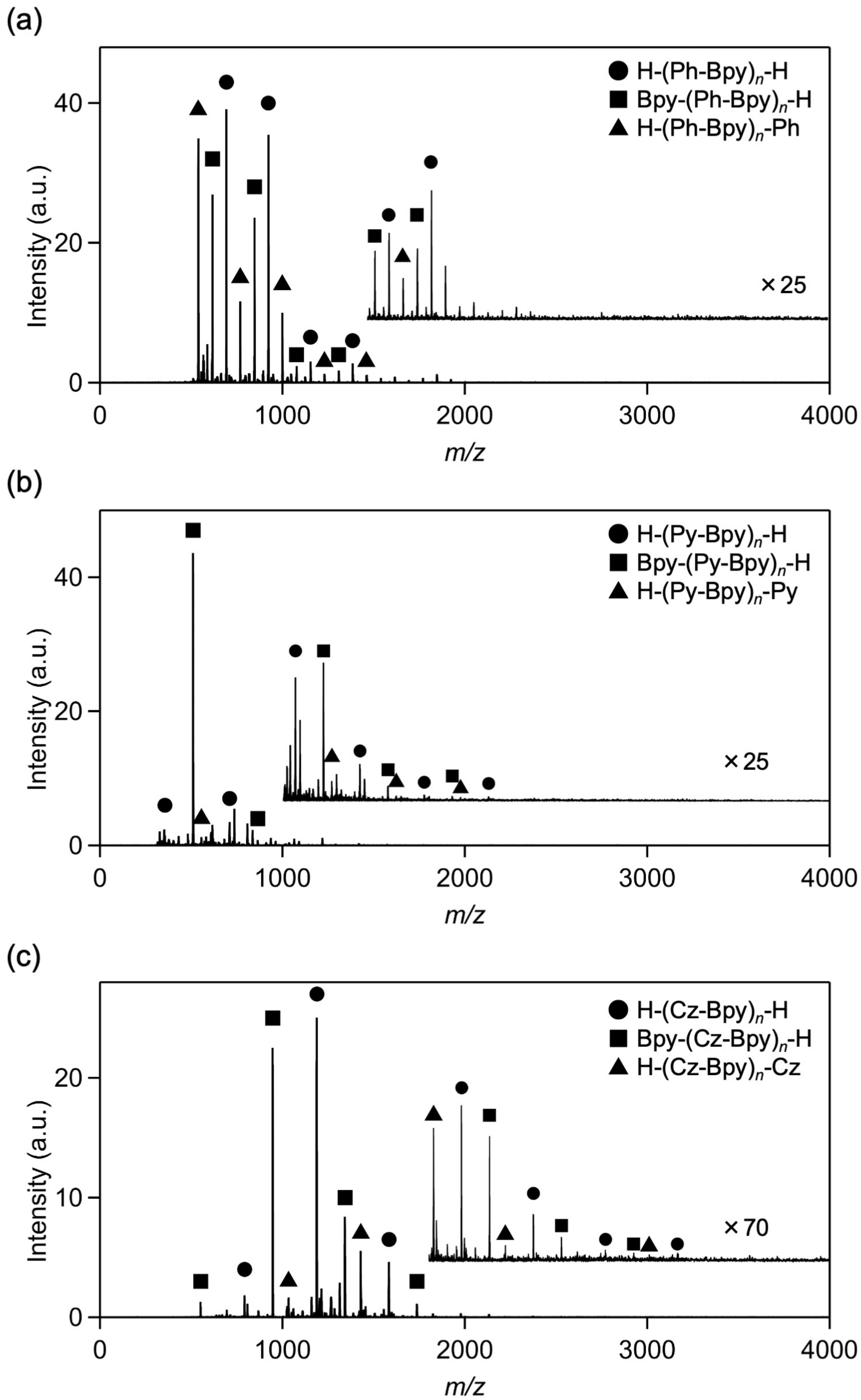

Fig. S1 MALDI-TOF-MS spectra of **[X-bpy]$_n$** (X = (a) Ph, (b) Py, or (c) Cz)

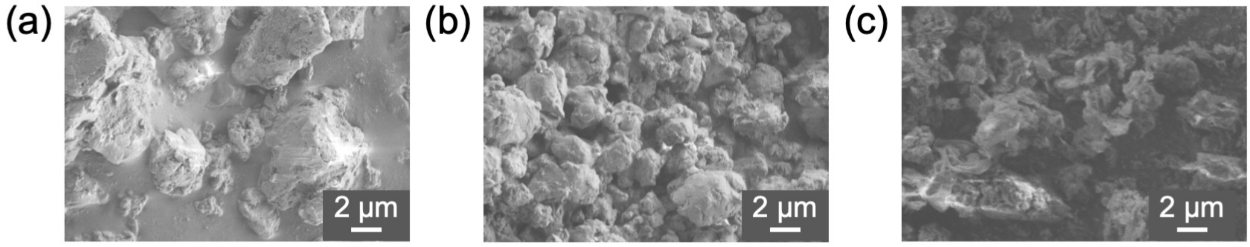

Fig. S2 SEM images of **[X-bpy]**$_n$ (X = (a) Ph, (b) Py, or (c) Cz).

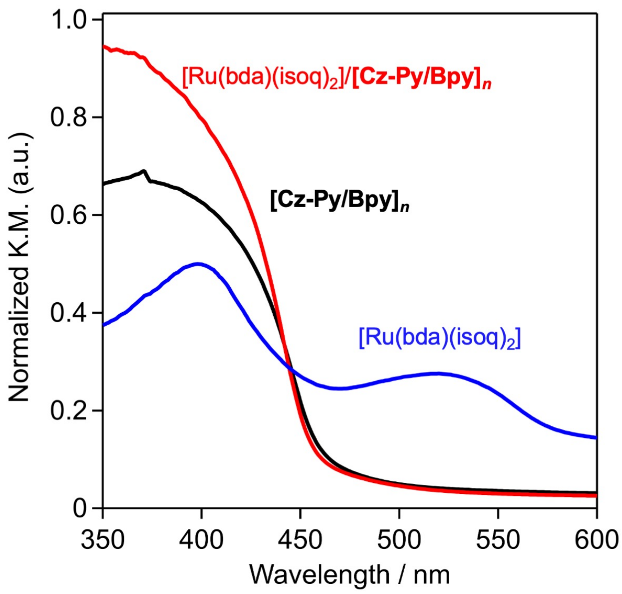

Fig. S3 UV-vis diffuse reflectance spectra of the polymer photocatalysts before (black line), after (red line) adsorption of [Ru(bda)(isoq)$_2$], along with that of [Ru(bda)(isoq)$_2$] (blue line).

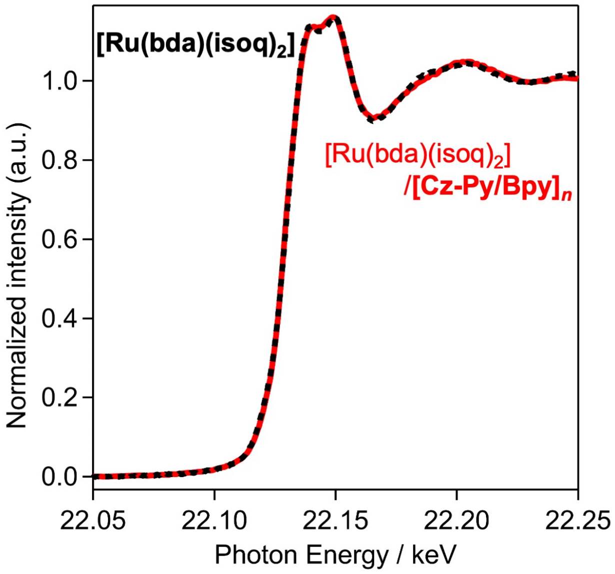

Fig. S4 Ru-K edge XANES spectra of [Ru(bda)(isoq)$_2$] (black dotted line) and **[Cz-Py/Bpy]$_n$** after adsorption of [Ru(bda)(isoq)$_2$] (red line).

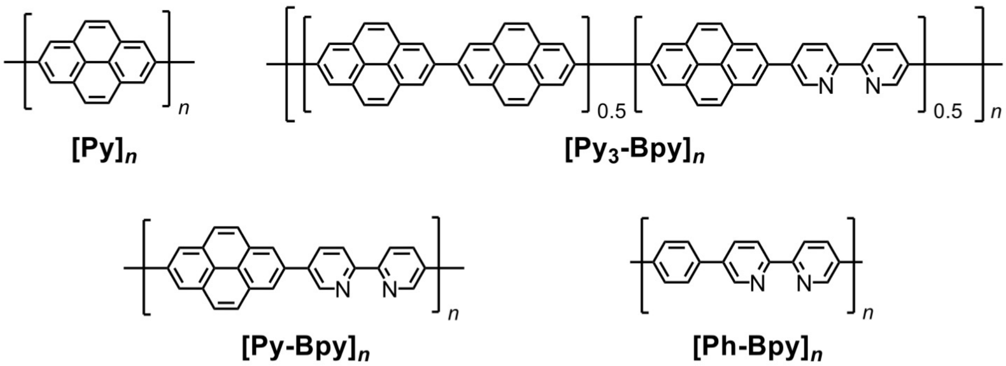

Fig. S5 Molecular structures of pyrene/bipyridine-based polymers with different pyrene contents.

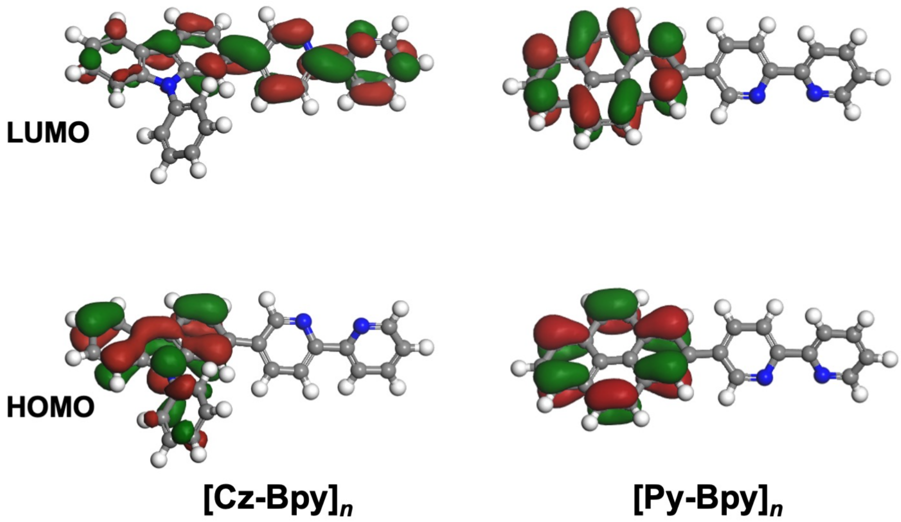

Fig. S6 Calculated HOMO (lower) and LUMO (upper) distributions of **X-bpy** (X = Cz, and Py).

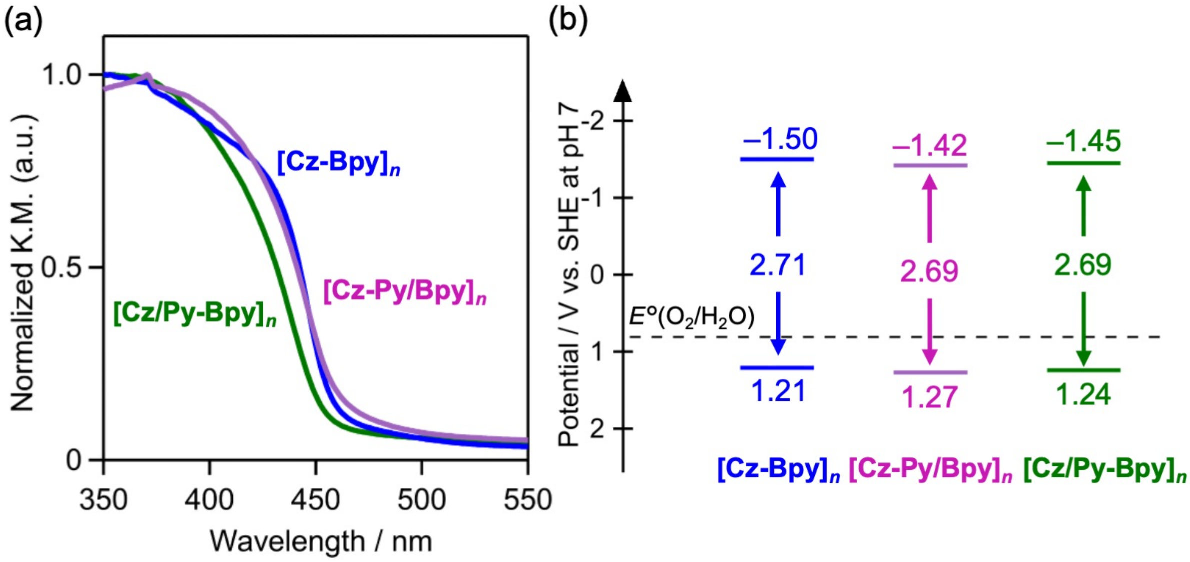

Fig. S7 (a) UV-vis diffuse reflectance spectra of the polymer photocatalysts and (b) HOMO-LUMO potentials of **[Cz-Bpy]**$_n$, **[Cz-Py/Bpy]**$_n$, and **[Cz/Py-Bpy]**$_n$.

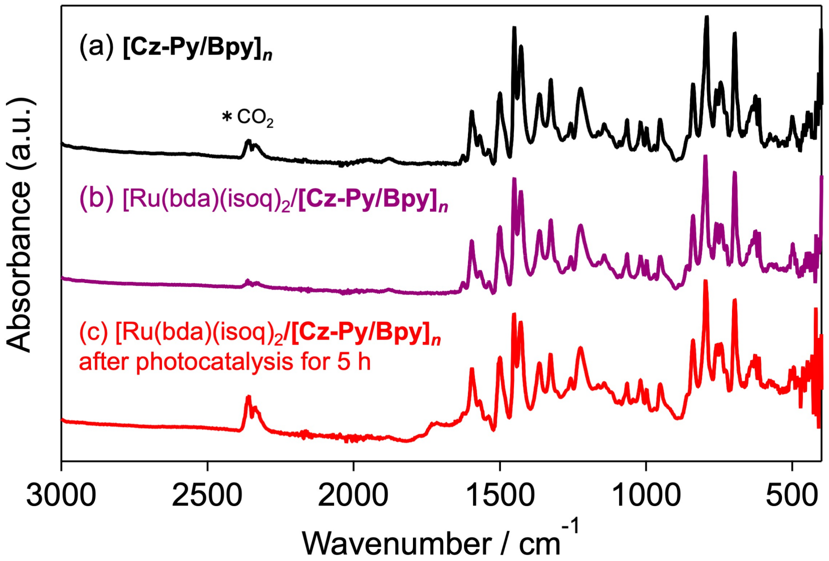

Fig. S8 ATR-IR spectra of (a) **[Cz-Py/Bpy]$_n$** and (b,c) [Ru(bda)(isoq)$_2$]/**[Cz-Py/Bpy]$_n$** before and after photocatalytic water oxidation for 5 h.

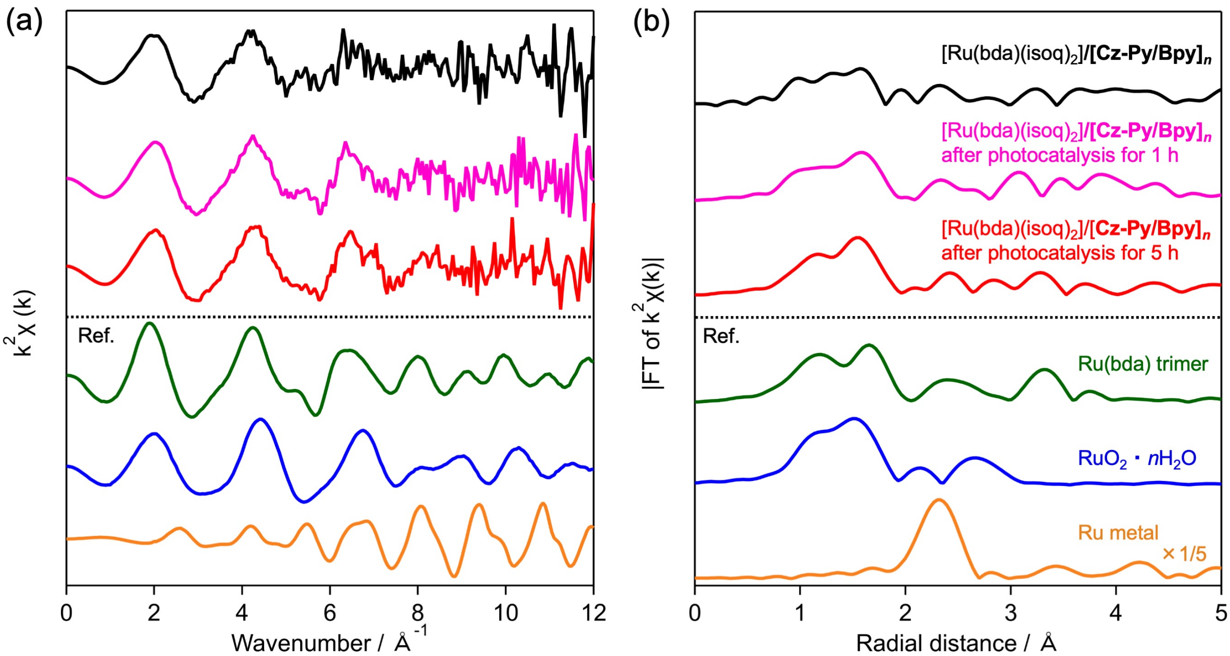

Fig. S9 (a) k^2-weighted Ru-K edge EXAFS spectra, and (b) their fourier transforms of [Ru(bda)(isoq)$_2$]/[**Cz-Py/Bpy**]$_n$ before and after photocatalytic water oxidation shown in Fig. 4, along with Ru metal, $RuO_2 \cdot nH_2O$, and Ru(bda) trimer complex as references.

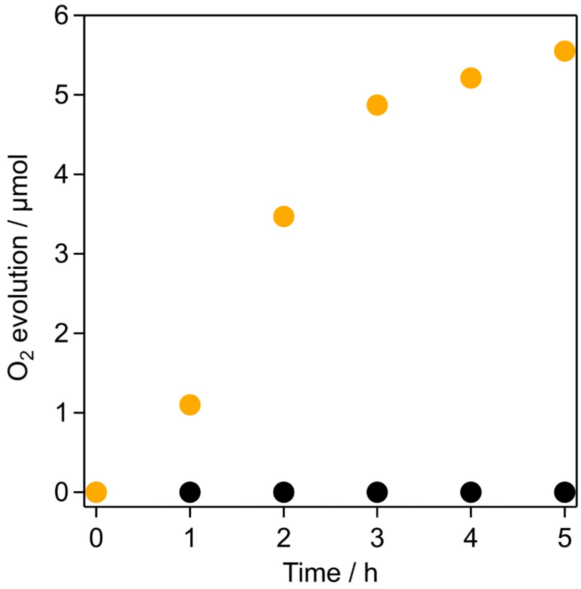

Fig. S10 Time courses of O_2 evolution over **[Cz-Py/Bpy]*n*** (50 mg) in aqueous $Na_2S_2O_8$ solution (10 mM, 50 mL) containing 10 μM [Ru(bda)(isoq)$_2$] (orange) or 10 μM $RuCl_3$ (black).

Table. S1 Photocatalytic CO_2 reduction under various conditions.[a]

			Product / μmol		
Entry	Photocatalyst	Control	Formate	CO	H_2
1	**[Cz-Py/BpyRu(CO)]*n***	—[a]	2.9	N.D.	0.8
2	**[Cz-Py/BpyRu(CO)]*n***	Without light	N.D.	N.D.	N.D.
3	**[Cz-Py/BpyRu(CO)]*n***	Without CO_2[b]	N.D.	N.D.	0.1
4	**[Cz-Py/BpyRu(CO)]*n***	Without sodium ascorbate	Trace	N.D.	0.3
5	**[Cz-Py/Bpy]*n***	—[a]	N.D.	N.D.	0.1

[a] Standard condition: 2 mg of photocatalyst powder in 10 mM sodium ascorbate aqueous solution dispersion was irradiated at $\lambda > 400$ nm for 10 h under CO_2 atmosphere. [b] Under Ar atmosphere.

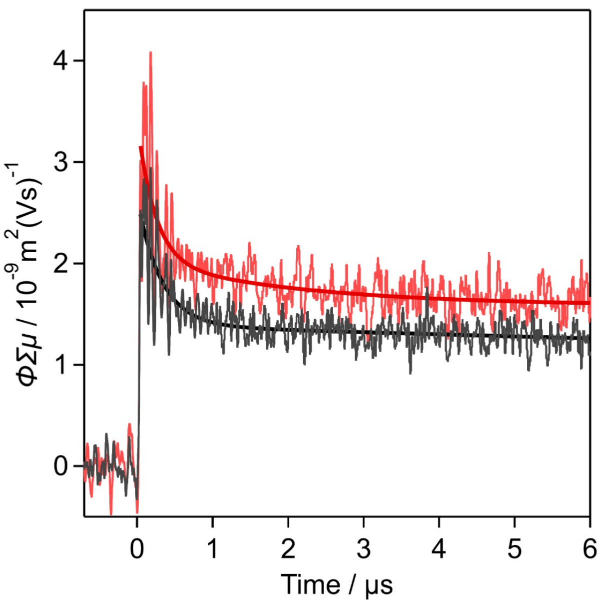

Fig. S11 Transient photoconductivities and their fittings using biexponential function ($A_1\exp(-k_1 t) + A_2\exp(-k_2 t)$) of **[Cz-Py/Bpy]*n*** (red) and **[Cz-Bpy]*n*** (black).

Table. S2 Overview of photocatalytic efficiency for water oxidation and CO_2 reduction using conjugated polymer-based photocatalysts in aqueous solution.

Abbreviation of Photocatalyst	Water oxidation			CO_2 reduction			Ref
	catalyst	electron acceptor	AQE (%)	catalyst	electron donor	AQE (%)	
[Py-Cz/Bpy]*n*	[Ru(bda)(isoq)$_2$]	$Na_2S_2O_8$	0.05 (430 nm)	(-bpy-)Ru(CO)$_2$Cl$_2$	Sodium ascorbate	0.02 (430 nm)	This work
TAPT-Bpy	Co^{2+}	$AgNO_3$	7.6 (420 nm)	Not demonstrated			[S1]
Bpy-CTF	Co^{2+}	$AgNO_3$	0.56 (420 nm)	Not demonstrated			[S2]
P10	Co	$AgNO_3$	–	Not demonstrated			[S3]
Bp-COF	Co^{2+}	$AgNO_3$	0.46 (420 nm)	Not demonstrated			[S4]
CTHP	Co	$AgNO_3$	–	Not demonstrated			[S5]
CTF-0-I	–	$AgNO_3$	5.2 (420 nm)	Not demonstrated			[S6]
g-$C_{40}N_3$	Co	$AgNO_3$	–	Not demonstrated			[S7]
CTF-1	RuO_x	$AgNO_3$	3.8 (420 nm)	Not demonstrated			[S8]
CTP-2	Co	$AgNO_3$	–	Not demonstrated			[S9]
aza-CMP	Co	$AgNO_3$	–	Not demonstrated			[S10]
g-C_3N_4	Co(OH)$_2$	$AgNO_3$	–	RuP complex	EDTA·2Na	–	[S11] [S12]

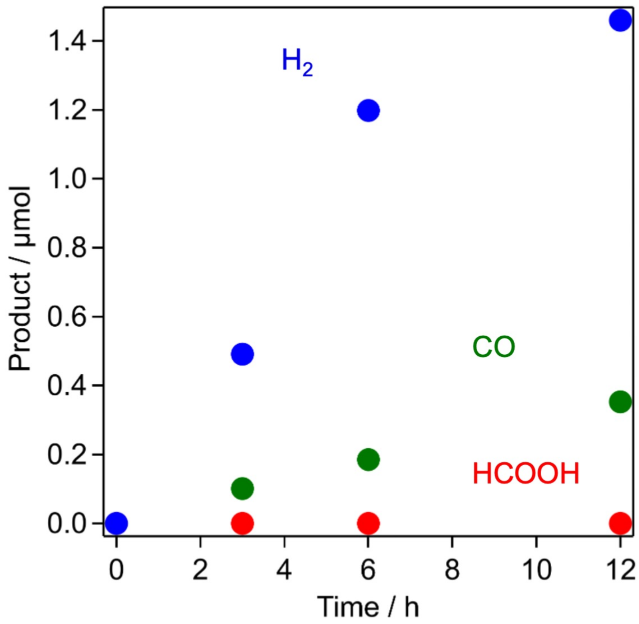

Fig. S12 Time courses of CO_2 reduction over [Ru(bda)(isoq)$_2$]/**[Cz-Py/BpyRu(CO)]*n*** hybrid (2 mg) in water (2 mL) (i.e., without sacrificial reagent) upon visible-light irradiation ($\lambda > 400$ nm).

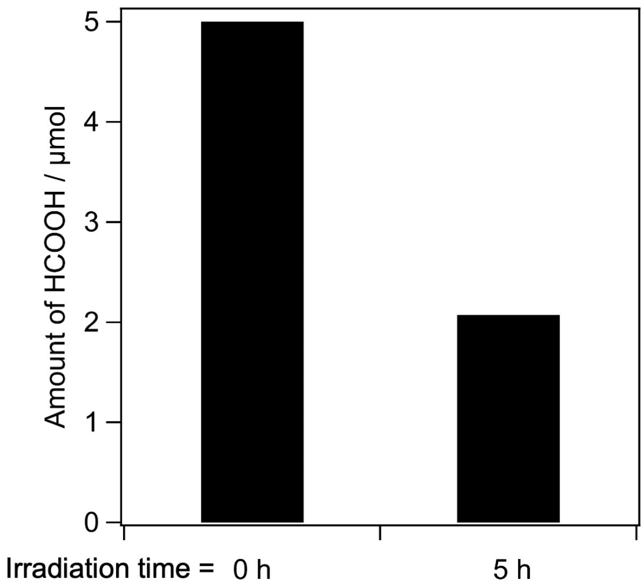

Fig. S13 The amount of HCOOH during water oxidation over [Ru(bda)(isoq)$_2$]/**[Cz-Py/Bpy]*n*** hybrid (5 mg) in 1 mM HCOOH aqueous solution (5 mL) upon visible-light irradiation ($\lambda = 430$ nm).

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