Supplementary Information

Photoexcited charge manipulation in conjugated polymers bearing a Ru(II) complex catalyst for visible-light CO₂ reduction

Akinobu Nakada,[*a,b] *Ryuichi Miyakawa,*[a] *Ren Itagaki,*[a] *Kosaku Kato,*[c] *Chinami Takashima,*[d]

Akinori Saeki,[e] *Akira Yamakata,*[c] *Ryu Abe,*[f] *Hiromi Nakai,*[d,g,h] *and Ho-Chol Chang*[*a]

[a]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

[b]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

[c]Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku-ku, Nagoya 468-8511, Japan.

[d]Waseda Research Institute for Science and Engineering (WISE) and Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.

[e]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.

[f]Department of Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

[g]Waseda Research Institute for Science and Engineering (WISE), Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.

[h]Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan.

*E-mail: nakada@scl.kyoto-u.ac.jp (A.N.), chang@kc.chuo-u.ac.jp (H.C.)

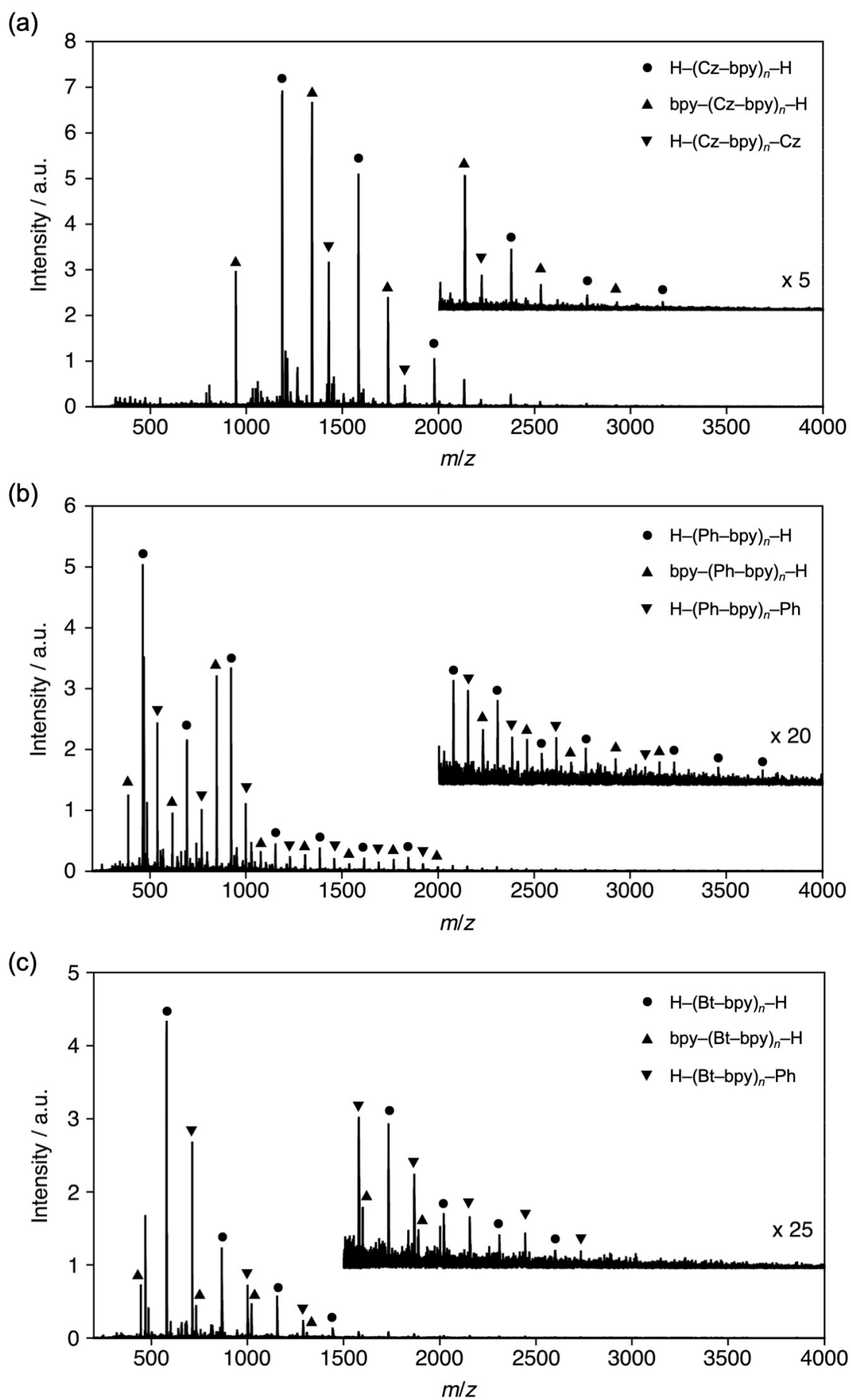Phone: +81-75-383-7044. Fax: +81-75-383-2479.

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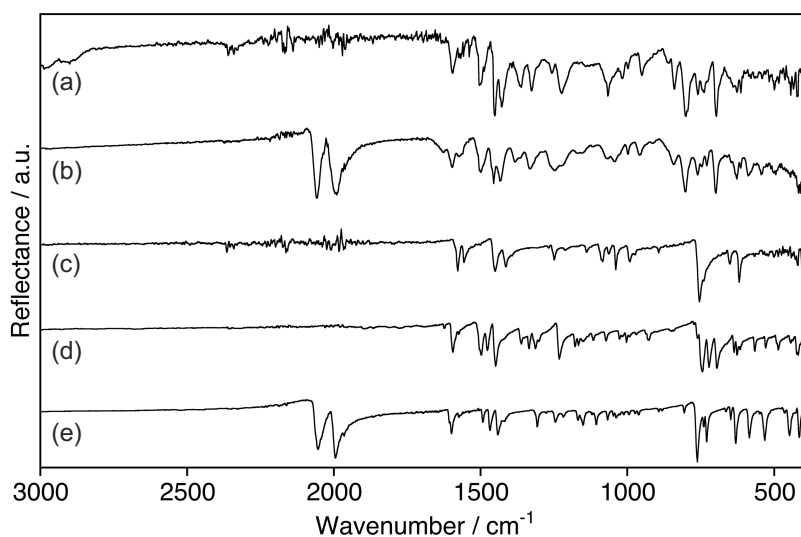**Fig. S1** MALDI-TOF-MS spectra of **[X-bpy]**$_n$ (X = (a) Cz, (b) Ph, or (c) Bt).

Fig. S2 ATR-IR spectra of **[Cz-bpyM]**$_n$ (M = (a) none or (b) Ru), (c) 2,2'-bipyridine, (d) 9-phenylcarbazole, and (e) Ru(bpy)(CO)$_2$Cl$_2$.

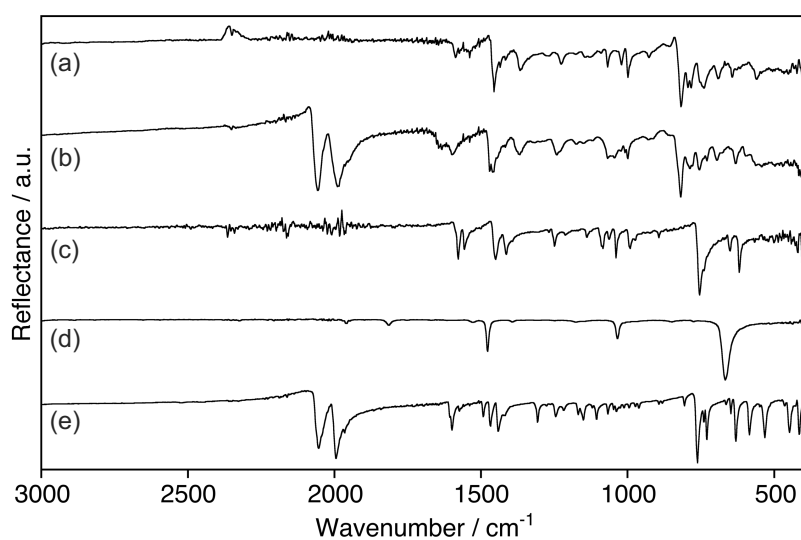**Fig. S3** ATR-IR spectra of **[Ph-bpyM]**$_n$ (M = (a) none or (b) Ru), (c) 2,2'-bipyridine, (d) benzene, and (e) Ru(bpy)(CO)$_2$Cl$_2$.

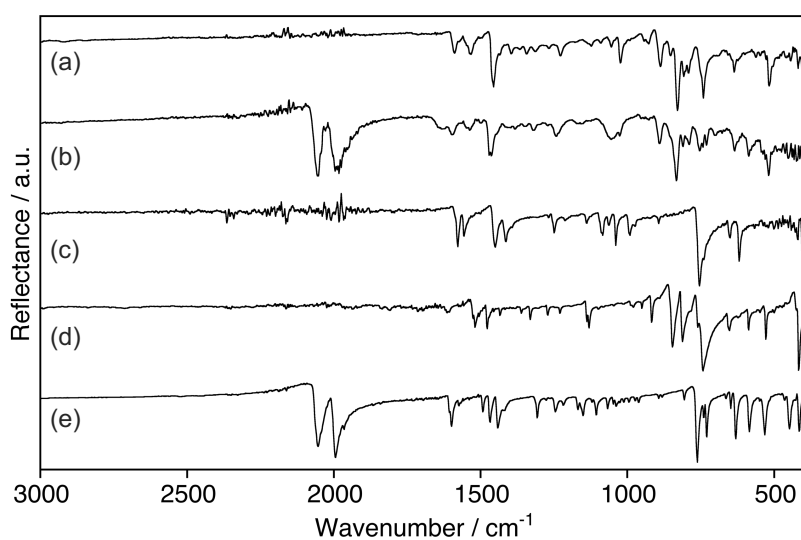**Fig. S4** ATR-IR spectra of **[Bt-bpyM]**$_n$ (M = (a) none or (b) Ru), (c) 2,2'-bipyridine, (d) 2,1,3-benzothiadiazole, and (e) Ru(bpy)(CO)$_2$Cl$_2$.
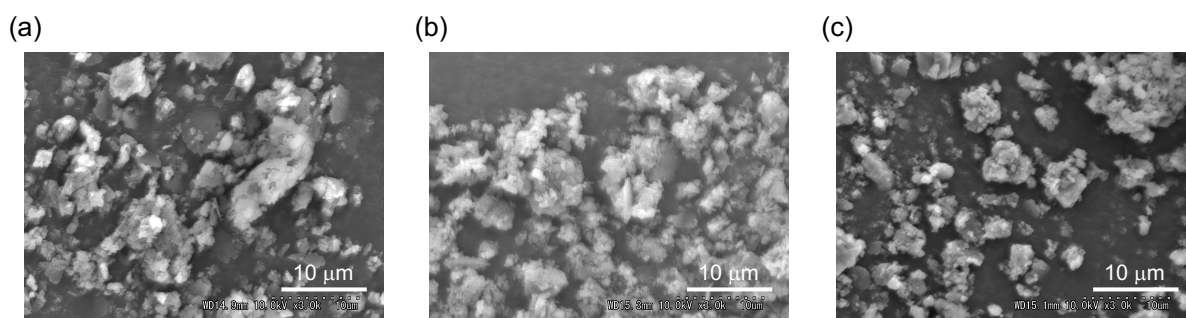
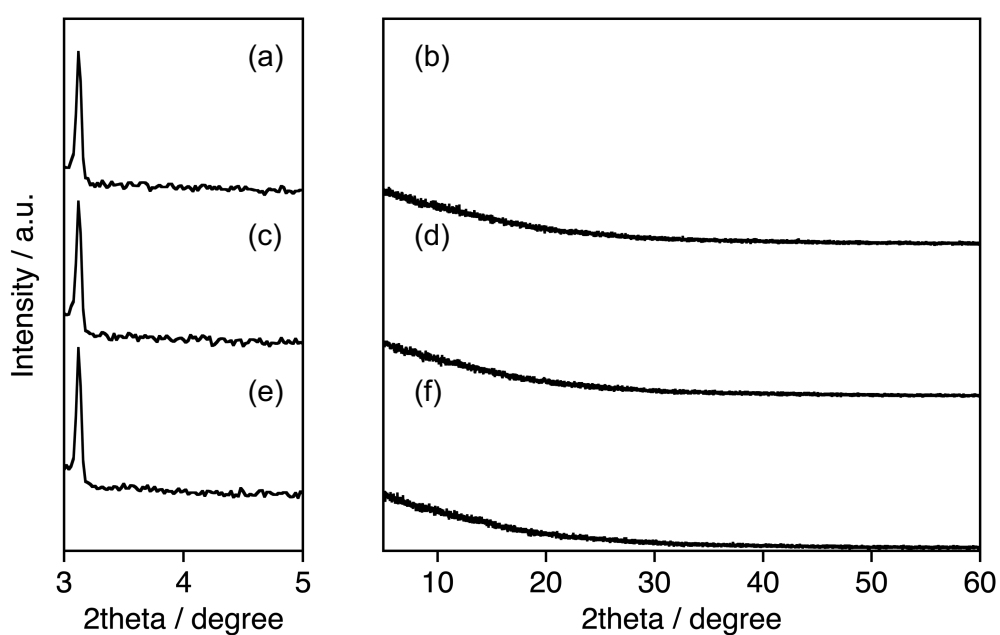**Fig. S5** SEM images of **[X-bpyRu]**$_n$ (X = (a) Cz, (b) Ph, or (c) Bt).

Fig. S6 XRD patterns of **[X-bpyRu]**$_n$ (X = (a,b) Cz, (c,d) Ph, or (e,f) Bt) in ranges of (a,c,e) 3-5 degree and (b,d,f) 5-60 degree.
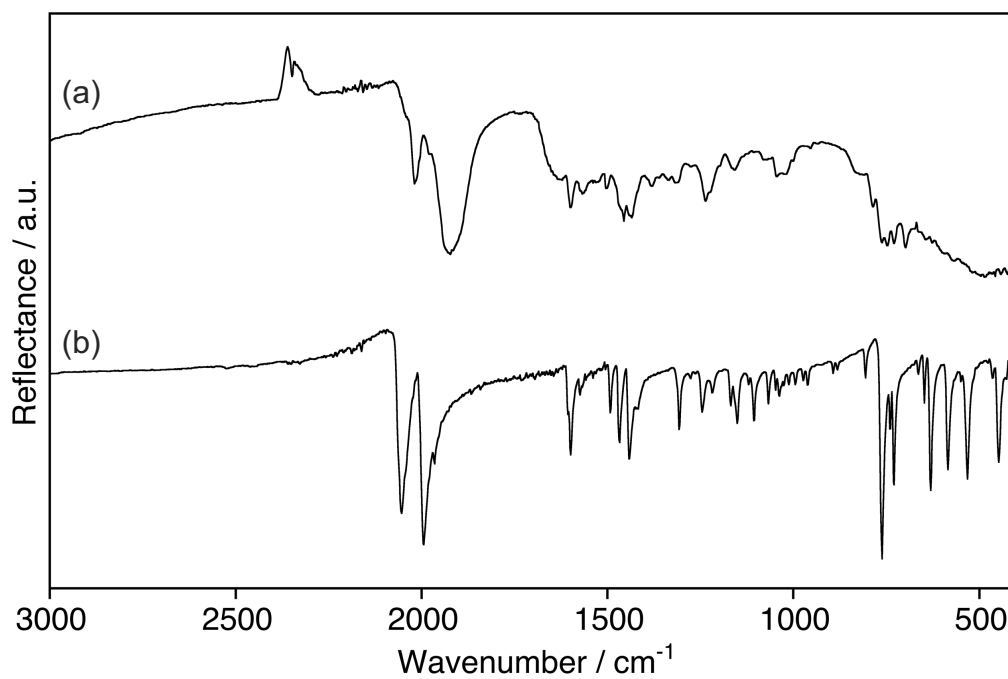
Fig. S7 ATR-IR spectra of (a) **[Cz-bpyRu]**$_n$, which is synthesized from Ru(Br$_2$bpy)(CO)$_2$Cl$_2$ and Cz-(B(OR)$_2$)$_2$, and (b) Ru(bpy)(CO)$_2$Cl$_2$.
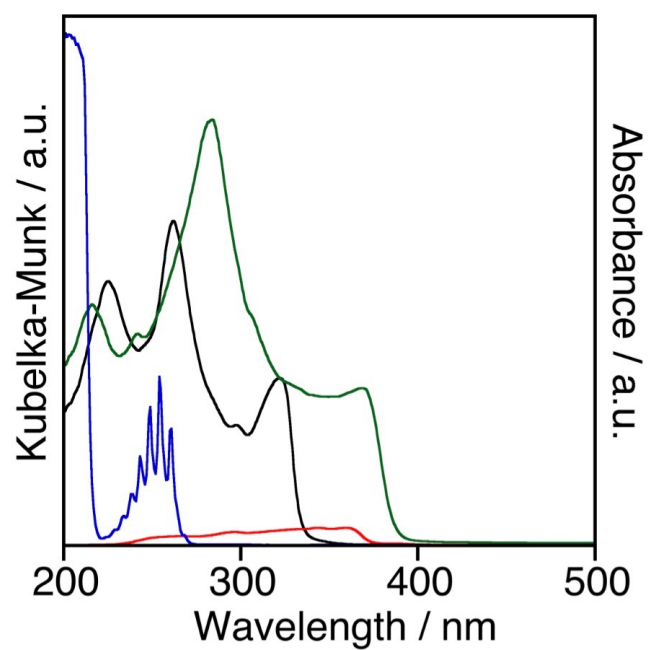
Fig. S8 UV-vis DRS of 2,2'-bipyridine (black), 9-phenylcarbazole (red), 2,1,3-benzothiadiazole (green), and UV-vis absorption spectrum of benzene in MeCN (blue).

Table R1. Charge distributions of **X-bpyRu** (X = Cz, Ph, and Bt) in the S_0 and T_1 states obtained by Mulliken population analysis. Δ represents the deviations of the T_1 values from the S_0 ones.

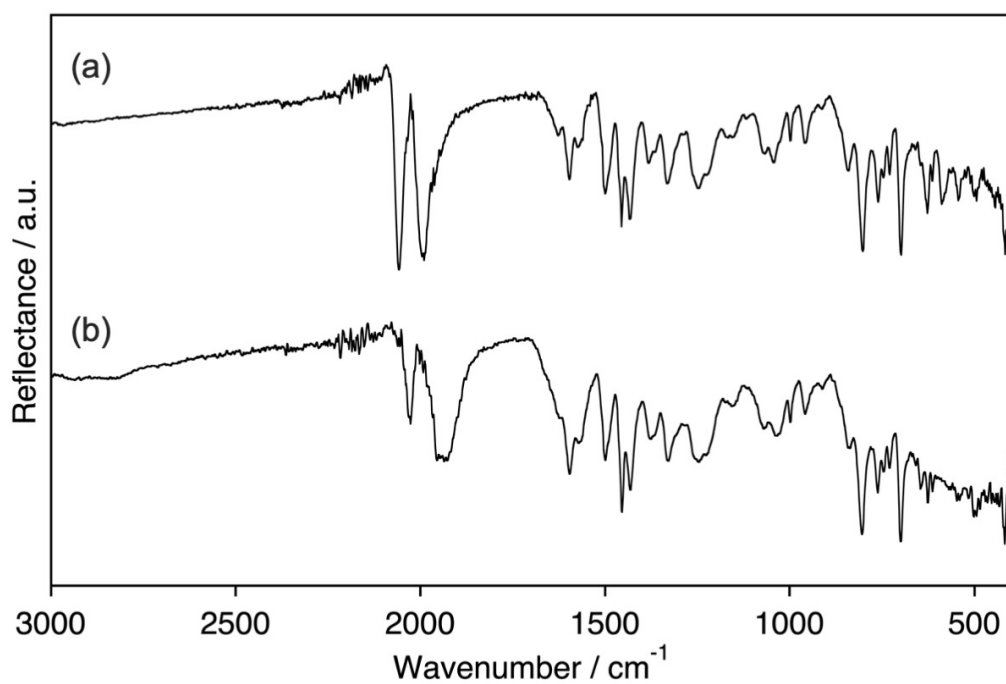|	Cz-bpyRu			Ph-bpyRu			Bt-bpyRu		
	S_0	T_1	Δ	S_0	T_1	Δ	S_0	T_1	Δ
X	0.072	0.129	0.057	0.051	0.051	−0.001	0.019	−0.002	−0.021
bpyM	−0.072	−0.129	−0.057	−0.051	−0.051	0.001	−0.019	0.002	0.021

Fig. S9 ATR-IR spectra of **[Cz-bpyRu]**$_n$ (a) before and (b) after photocatalysis at $\lambda > 400$ nm for 12 h.
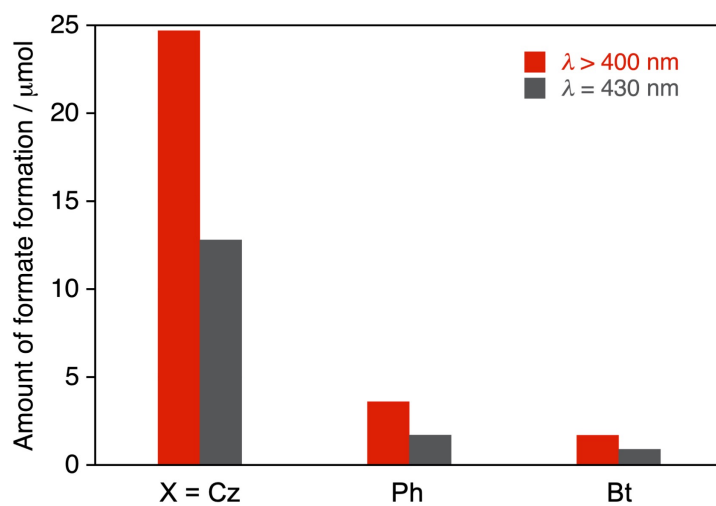
Fig. S10 Photocatalytic activities of **[X-bpyRu]**$_n$ for formate formation under a CO_2 atmosphere upon irradiation at $\lambda > 400$ nm (red) or $\lambda = 430$ nm (gray). 2 mg of each photocatalyst powder in an MeCN-TEOA (2 mL; 4:1 *v/v*) dispersion was irradiated for 12 h.