Supplementary Information

Strong impacts of inter-π-chain charge transfer accelerating CO_2 reduction photocatalysis of carbazole–diimine-based linear conjugated polymer/Ru complex hybrids

Akinobu Nakada,[a,b]* *Shunsuke Asai,*[a] *Chen Zhang,*[a] *Kotaro Ishihara,*[a] *Hajime Suzuki,*[a]

Osamu Tomita,[a] *Katsuaki Suzuki,*[c] *Hironori Kaji,*[c] *Akinori Saeki,*[d] *and Ryu Abe*[a]*

[a] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, 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] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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

*E-mail: nakada@scl.kyoto-u.ac.jp (A.N.), ryu-abe@scl.kyoto-u.ac.jp (R.A.)

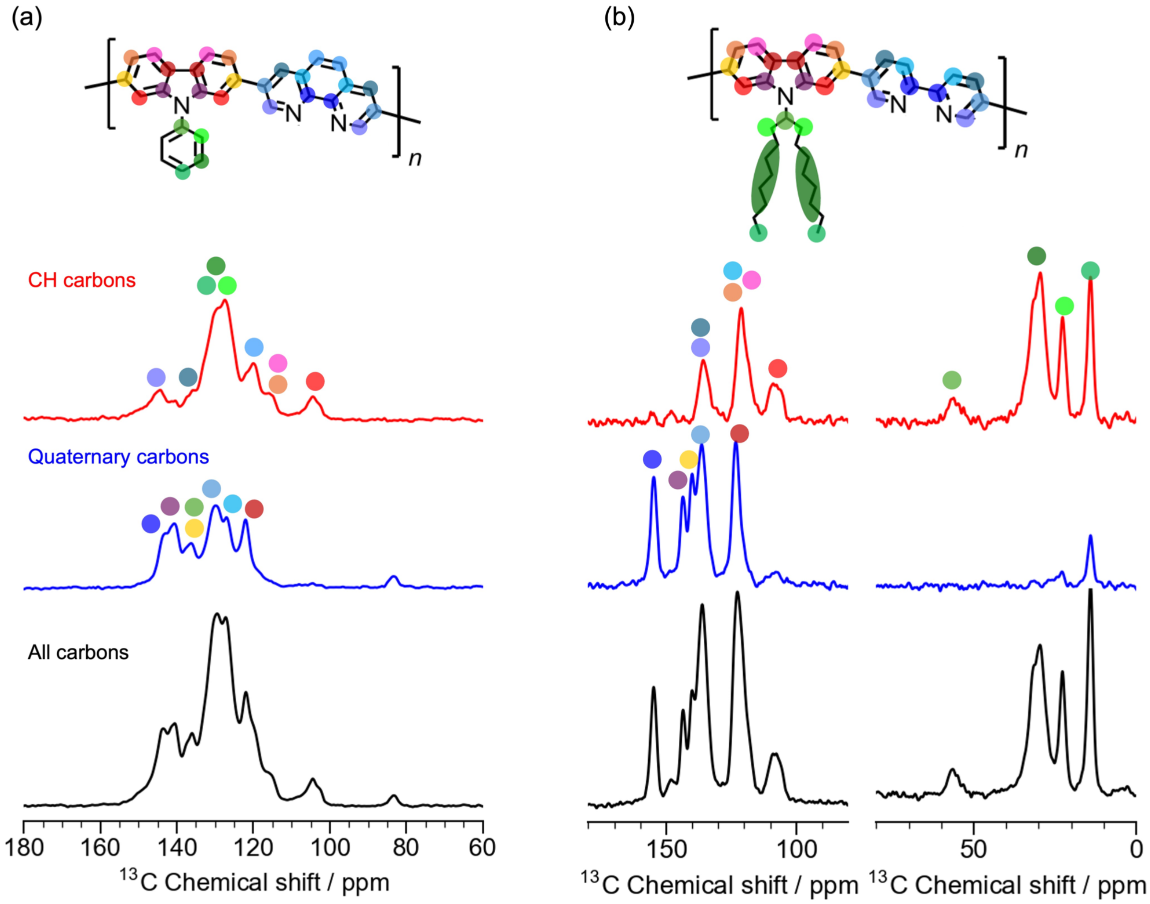

Fig. S1 Solid-state ^{13}C cross polarization/magic angle spinning (CP/MAS) spectra of (a) **[PhCz-Phen]$_n$** and (b) **[C$_{8,8}$Cz-Bpy]$_n$**. Assignments were made based on gauge-independent atomic orbital (GIAO) calculations. In the CP/MAS experiments, a ^{1}H 90° pulse of 3 μs (83.3 kHz) was first applied, followed by a CP process with ^{1}H and ^{13}C field strengths of 71.4 kHz and a contact time of 4 ms. SPINAL64 ^{1}H dipolar decoupling with ^{1}H field strength of 83.3 kHz was applied during the detection of free induction decay. The recycle delay and the MAS frequency were set to 4 s and 20 kHz, respectively. A total of 4096 transients were accumulated for each measurement. The ^{13}C NMR spectra of quaternary carbons (blue) were measured selectively using the dipolar dephasing technique with a ^{1}H–^{13}C dipolar dephasing time of 1.0 ms for the aromatic region and 6.0 ms for the aliphatic region with a 180° pulse in the middle of the dephasing time. The spectra of CH carbons (red) were obtained by subtracting those of quaternary carbons (blue) from all carbons (black).

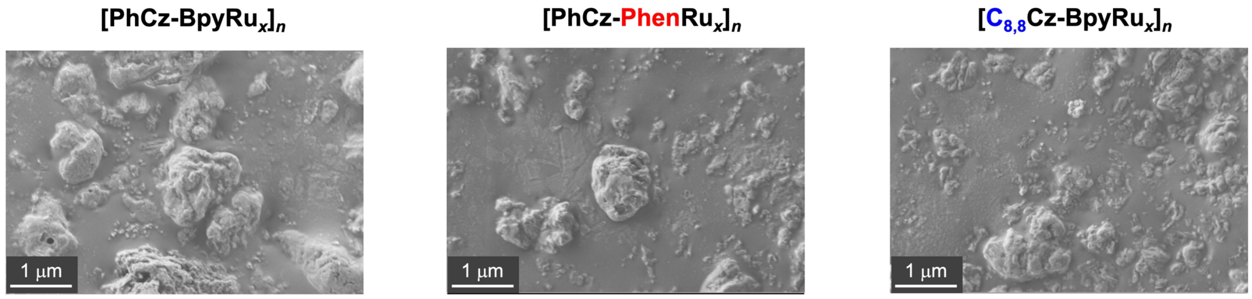

Fig. S2 SEM images of **[PhCz-Bpy]$_n$**, **[PhCz-Phen]$_n$**, and **[C$_{8,8}$Cz-Bpy]$_n$**.

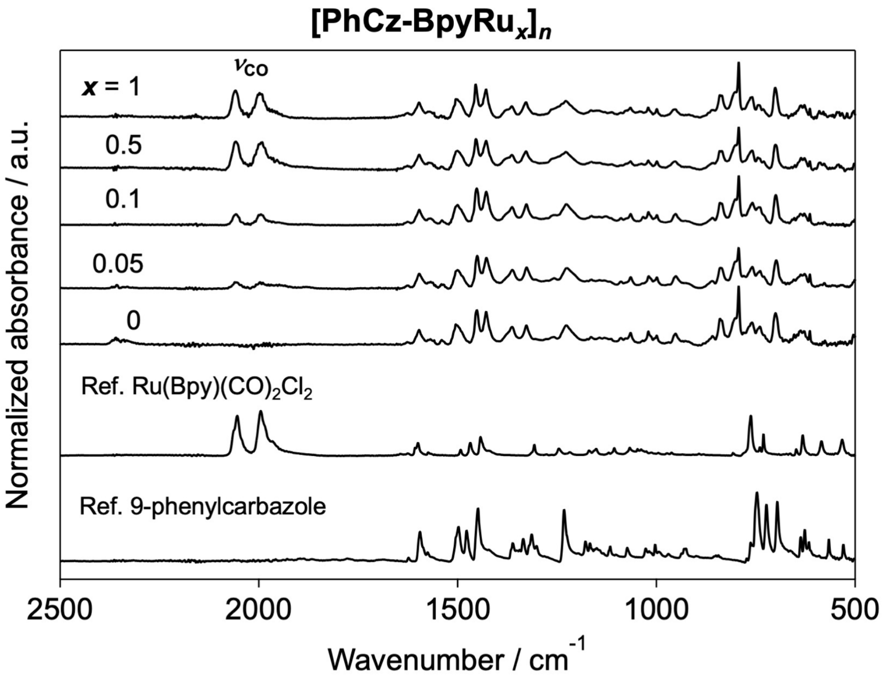

Fig. S3 ATR-FT-IR spectra of **[PhCz-BpyRu$_x$]$_n$** along with reference compounds.

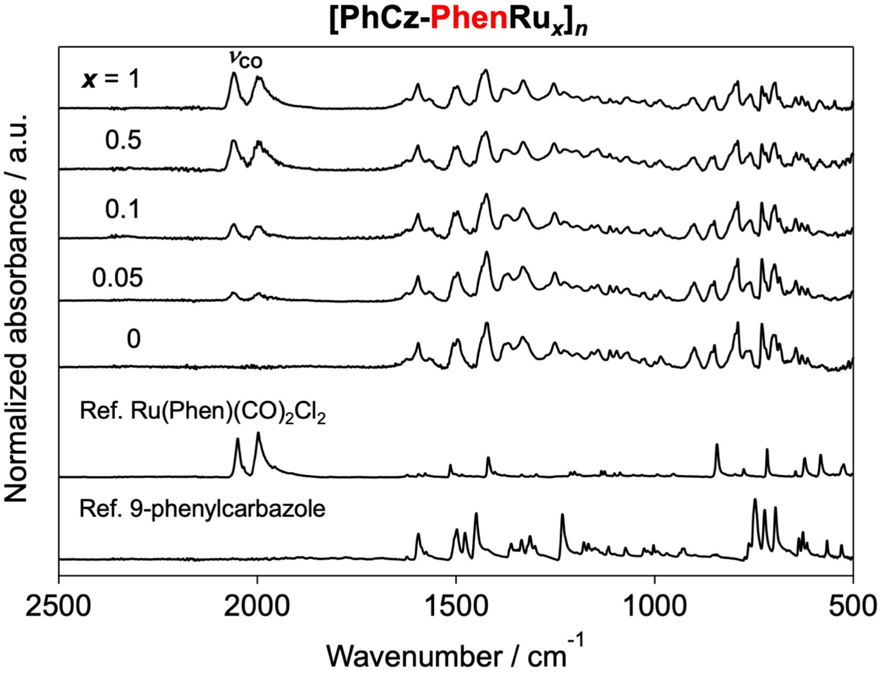

Fig. S4 ATR-FT-IR spectra of **[PhCz-PhenRu$_x$]$_n$** along with reference compounds.

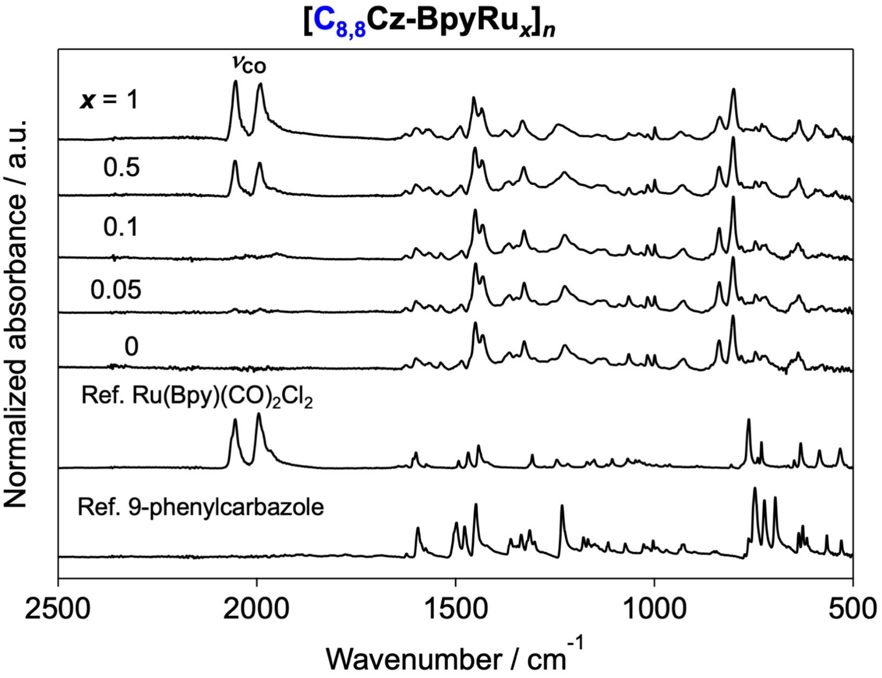

Fig. S5 ATR-FT-IR spectra of **[C$_{8,8}$Cz-BpyRu$_x$]$_n$** along with reference compounds.

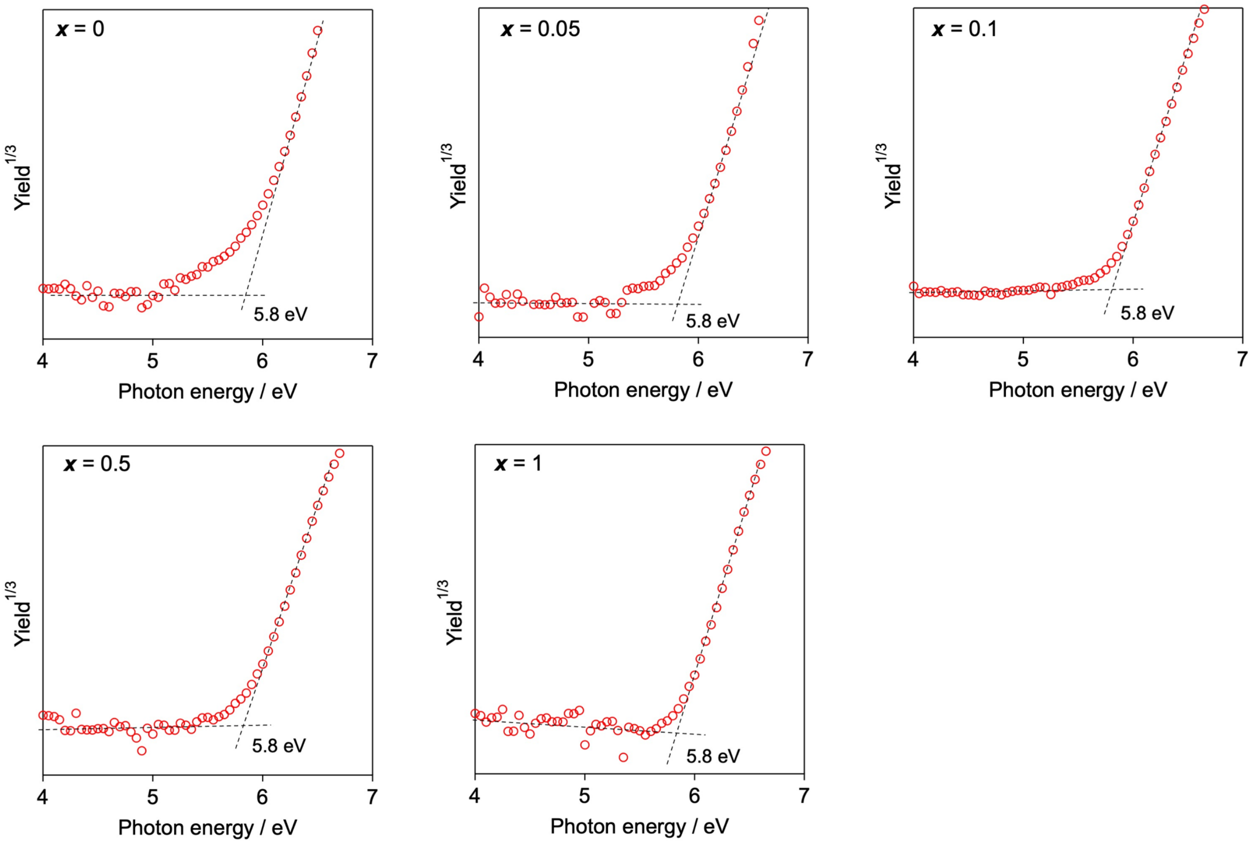

Fig. S6 Photoelectron yield spectra of **[PhCz-BpyRu$_x$]$_n$**,.

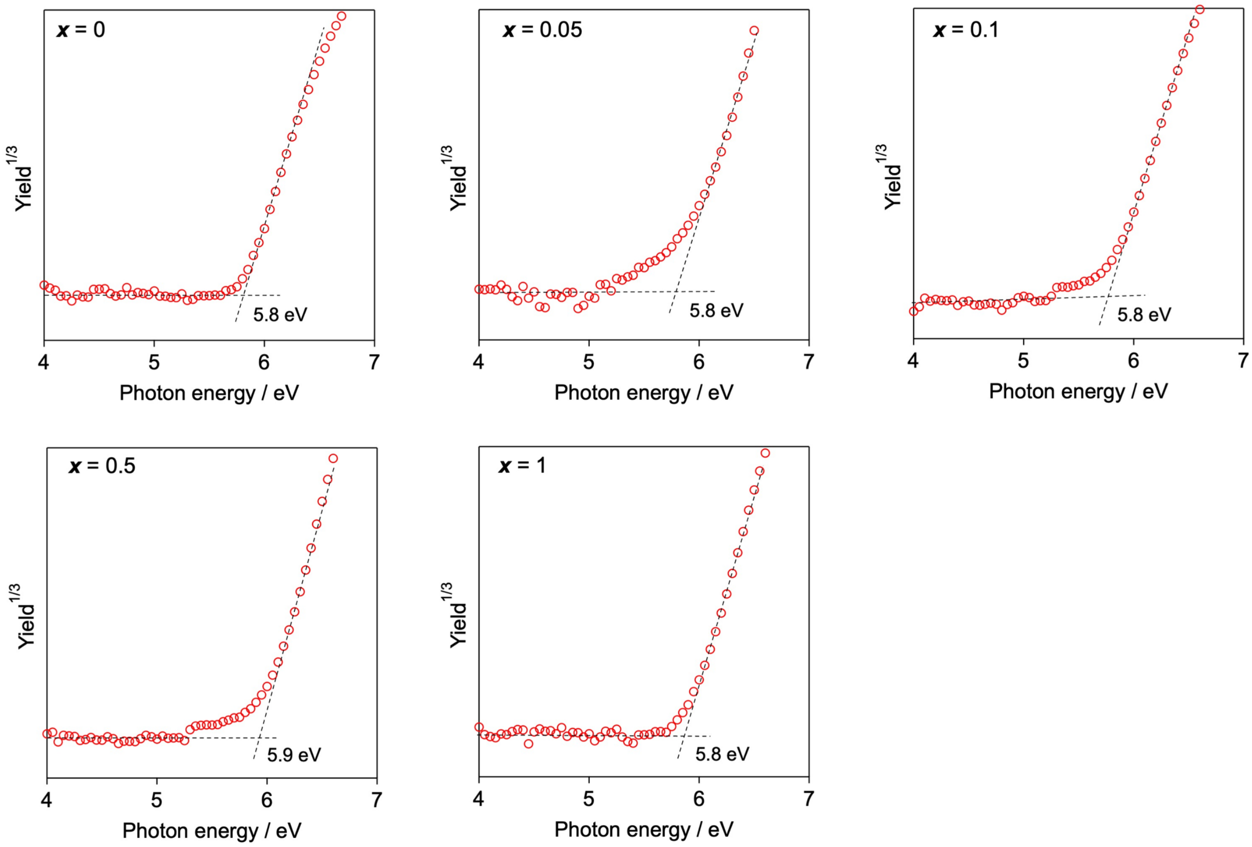

Fig. S7 Photoelectron yield spectra of **[PhCz-PhenRu$_x$]$_n$**.

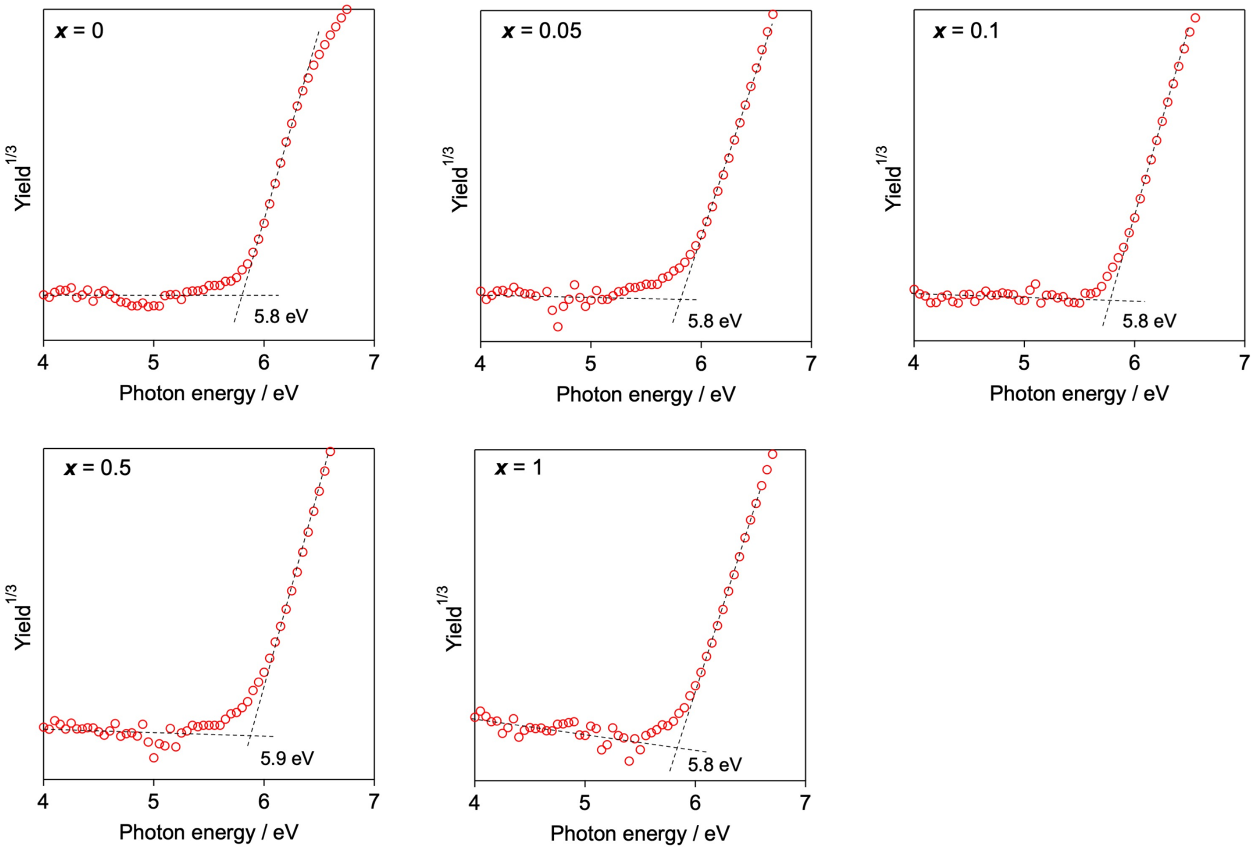

Fig. S8 Photoelectron yield spectra of $\mathbf{[C_{8,8}Cz\text{-}BpyRu_{\mathit{x}}]_{\mathit{n}}}$.

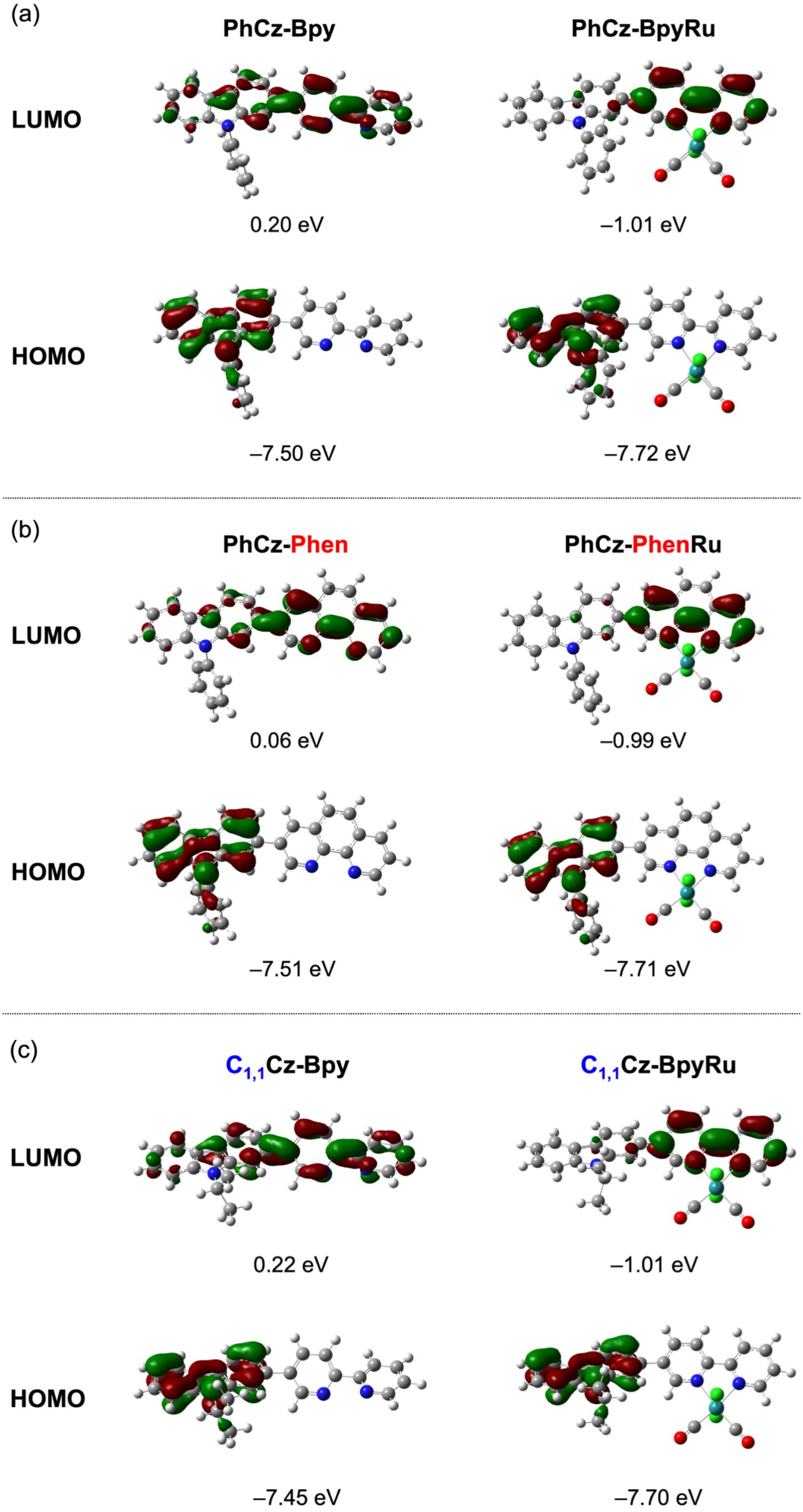

Fig. S9 Calculated HOMO (lower) and LUMO (upper) distributions and energies of (a) **PhCz-Bpy** and **PhCz-BpyRu**, (b) **PhCz-Phen** and **PhCz-PhenRu**, (c) **C$_{1,1}$Cz-Bpy** and **C$_{1,1}$Cz-BpyRu**. **C$_{1,1}$Cz-BpyM** was calculated as a model for **C$_{8,8}$Cz-BpyM** by omitting long alkyl chains.

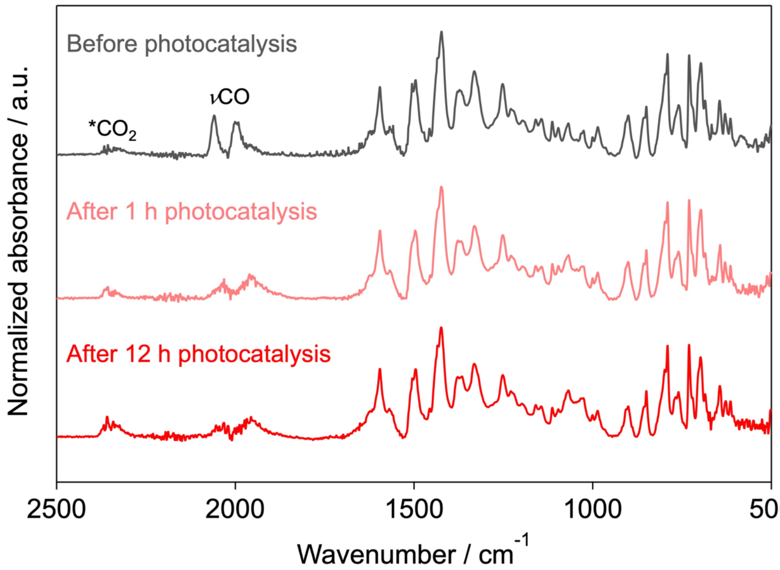

Fig. S10 ATR-FT-IR spectra of **[PhCz-PhenRu$_{0.1}$]$_n$** before and after photocatalysis for 1 and 12 h.

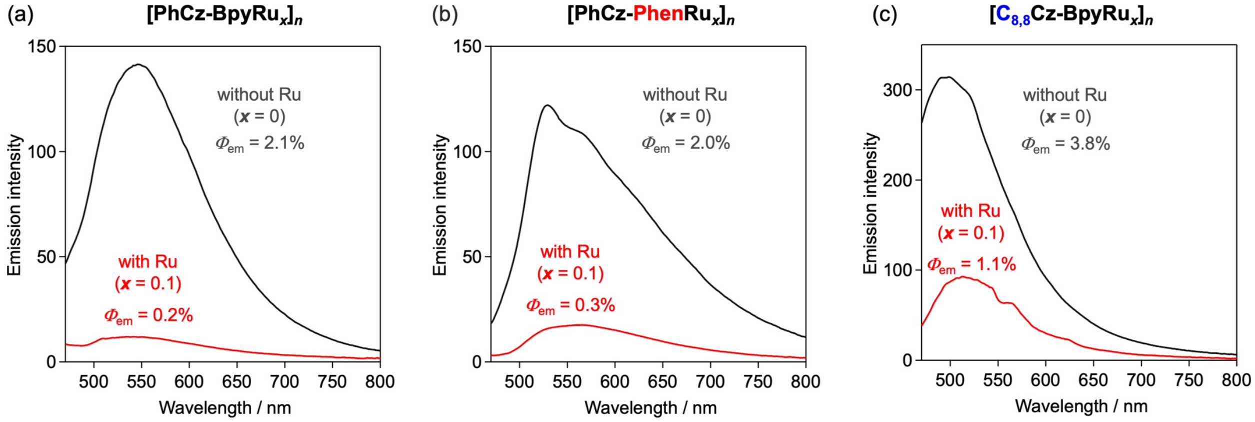

Fig. S11 Emission spectra of (a) **[PhCz-BpyRu$_x$]$_n$**, (b) **[PhCz-PhenRu$_x$]$_n$**, and (c) **[C$_{8,8}$Cz-BpyRu$_x$]$_n$** excited at $\lambda = 440$ nm in acetonitrile dispersion under Ar atmosphere.

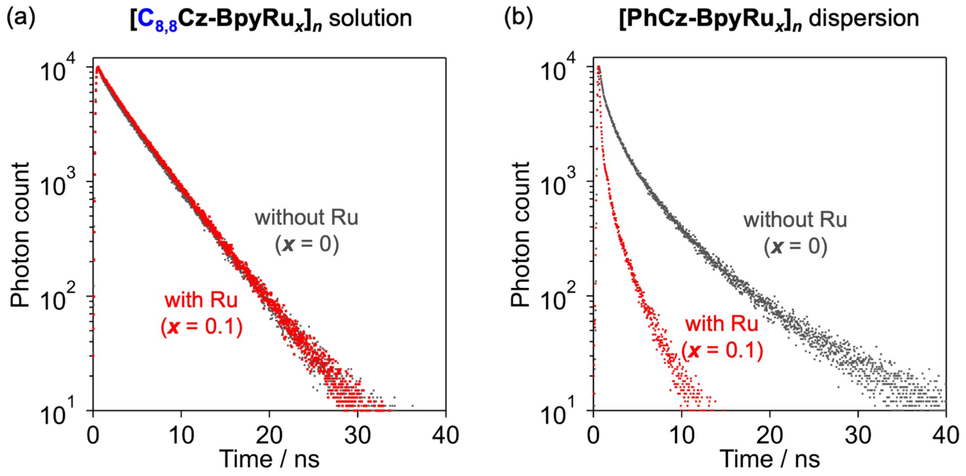

Fig. S12 Emission decays of (a) **[C$_{8,8}$Cz-BpyRu$_x$]$_n$** (x = 0 or 0.1) in dichloromethane solution and (b) **[PhCz-BpyRu$_x$]$_n$** (x = 0 or 0.1) in dichloromethane dispersion excited at λ = 440 nm under Ar atmosphere.