

Supporting Information

Porous Organic Polymer Riched in Re Functional Units and Lewis Base Sites for Efficient CO₂ Photoreduction

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1. Reagents

Acetonitrile (CH_3CN , Aladdin), Dimethyl sulfoxide (DMSO, Aladdin) were of HPLC grade. Triethanolamine (TEOA, $\geq 99\%$) was obtained from Adamas. 2,2'-Bipyridine-5,5'-dicarbaldetetracarboxylchlororhenium(I) and $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ were synthesized according to the literature report^{1,2}. Other reagents were of analytical grade. All commercial chemicals were used without further purification.

2. Characterization

Fourier Transform Infrared (FT-IR) spectra were measured with KBr pellets on a Bruker IFS-66 V/S FT-IR spectrometer. ^{13}C Solid state Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 600 WB spectrometer operated at 600 MHz. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was conducted on Agilent 725. The method of dissolving BTN-Re: 10 mg BTN-Re and 5 mL nitric acid were put into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 24 h. X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALAB250 spectrometer with an excitation source of Mg $\text{K}\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out on pre-weighed samples in a nitrogen stream through Netzsch STA 449C apparatus from room temperature to 800 °C at a heating rate of 10 °C min^{-1} . Scanning electron microscopy (SEM) was conducted using JEOL JSM-7800F. Transmission electron microscopy (TEM) was performed using FEI Tecnai G2 S-Twin with a field emission gun operated at 200 kV. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping were performed on JEM-2100F. Gas sorption measurement was conducted using a Micromeritics ASAP 2020 system at desired temperatures. Before gas adsorption measurements, the samples were heated at 150 °C for 12

h. UV–vis diffuse reflectance spectra (UV–vis DRS) were carried out through PerkinElmer Lambda 850, with BaSO₄ as reference. Steady-state photoluminescence (PL) emission spectra and time-resolved PL data were recorded on an Edinburgh FLS920 fluorescence spectrometer in air at room temperature, and all the samples were tested in solid state.

3. Instruments used in photocatalysis experiments.

Photocatalytic reaction was carried out in a Lab Solar-III AG system (Perfectlight Limited, Beijing). A 300 W Xe lamp (PLS-SXE300, Perfectlight Limited, Beijing) was employed as light source, which was equipped with two cut filters to remove light with wavelengths less than 400 nm and longer than 780 nm. Light intensity was maintained at 400 mW/cm², which was detected by PL-MW2000 Photoradiometer (Perfectlight Limited, Beijing).

Gas products were analyzed by gas chromatography (GC, Techcomp, GC7900) with a flame ionization detector (FID, for detecting CO and CH₄) and a thermal conductivity detector (TCD, for detecting H₂). Liquid products were analyzed by ¹H-NMR (Bruker AVANCE III spectrometer at 600 MHz) spectrum. Gas products of the isotope tracer experiment were analyzed by gas chromatography mass spectrometry (GC-MS, Agilent, 5977B GC/MSD).

4. Qualitative detection of liquid products³.

500 μL supernatant after catalytic reaction (filtered by a filter) was mixed with 100 μL CD₃CN (acetonitrile-d₃). Then, the mixed solution was analyzed by NMR spectroscopy. In order to further demonstrate the liquid products, a control solution was prepared, in which 45 mL CH₃CN, 5 mL TEOA, 20 μL CH₃OH, 20 μL HCOOH were mixed uniformly. 100 μL CD₃CN was added to 500 μL above control solution before it was analyzed by NMR spectroscopy.

5. Electrochemical characterization.

Electrochemical measurements were conducted with a BioLogic (France) Electrochemical System in a conventional three-electrode cell, using a platinum wire as the counter electrode and a saturated calomel electrode as the reference electrode. To prepare the working electrode, 5 mg BTN-Re was mixed with 0.5 mL Nafion (5% w/w in water and 1-propanol) and sonicated for 30 min. Then the slurry was dropwise coated to the surface of a rotating fluoride–tin oxide glass plate (covering approximately 1 cm²) and dried in the air. The experiments were performed in 0.1 M Na₂SO₄ electrolyte at room temperature.

6. The theoretical content of Re in BTN-Re and the theoretical content of bipyridine units coordinated with Re.

Theoretically, when all functional groups are involved in the reaction, the ratio of melamine to BPDA in BTN is 4:3, and the molecular formula of BTN can be written as [(C₃N₆H₃)₄(C₁₂N₂H₈)₃]_n.

The highest theoretical content of Re can be calculated as follows:

$$C_{\text{Re}} = \frac{3 * M[\text{Re}]}{3 * M[\text{Re}(\text{CO})_3\text{Cl}] + M[(\text{C}_3\text{N}_6\text{H}_3)_4(\text{C}_{12}\text{N}_2\text{H}_8)_3]} = 28.6\% \quad (1)$$

M[Re]: the relative atomic mass of Re (186.207 g/mol).

M[Re(CO)₃Cl]: the relative mass of Re(CO)₃Cl (305.690 g/mol).

M[(C₃N₆H₃)₄(C₁₂N₂H₈)₃]: the relative mass of the smallest unit representing BTN (1023.999 g/mol).

Assuming that the content of the bipyridine units coordinated with Re is ω, according to the actual content of Re is 15.33%, the equation can be listed as follows:

$$\frac{3 * \omega * M[\text{Re}]}{3 * \omega * M[\text{Re}(\text{CO})_3\text{Cl}] + M[(\text{C}_3\text{N}_6\text{H}_3)_4(\text{C}_{12}\text{N}_2\text{H}_8)_3]} = 15.33\% \quad (2)$$

$$\omega = 37.9\%$$

The content of the bipyridine units coordinated with Re is 37.9%.

7. The calculation of TON

Re is chelated by bipyridine in the form of a “single Re⁺ ion”. Therefore, the amount of Re is the amount of the active sites. According to the result of photocatalytic reaction, TON can be calculated as follows:

$$\text{TON} = \frac{n(\text{CO}_2)}{n(\text{Re})} = \frac{\frac{m[\text{BTN-Re}] * v[\text{BTN-Re}] * T}{m[\text{BTN-Re}] * \Omega[\text{Re}]}}{M[\text{Re}]} = 4.87 \quad (3)$$

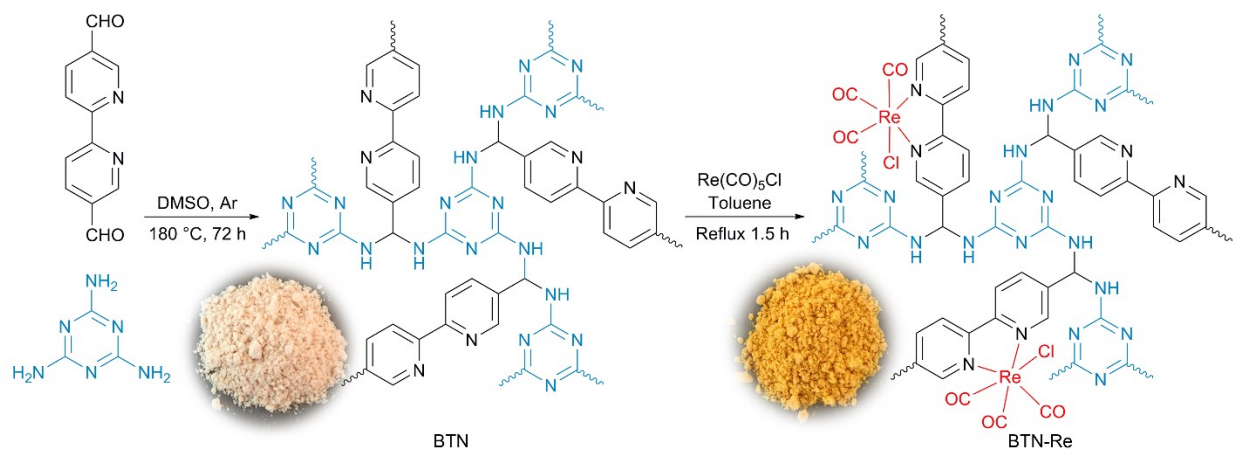
$m[\text{BTN-Re}]$: the mass of BTN-Re used in the catalytic reaction (10 mg).

$v[\text{BTN-Re}]$: CO evolution rate (500.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$).

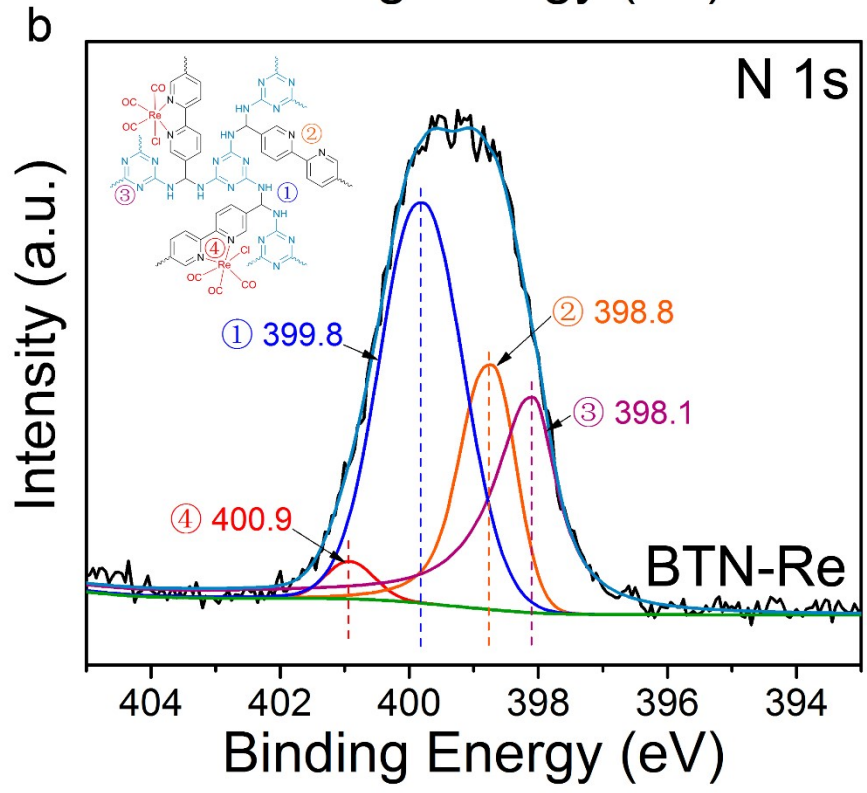
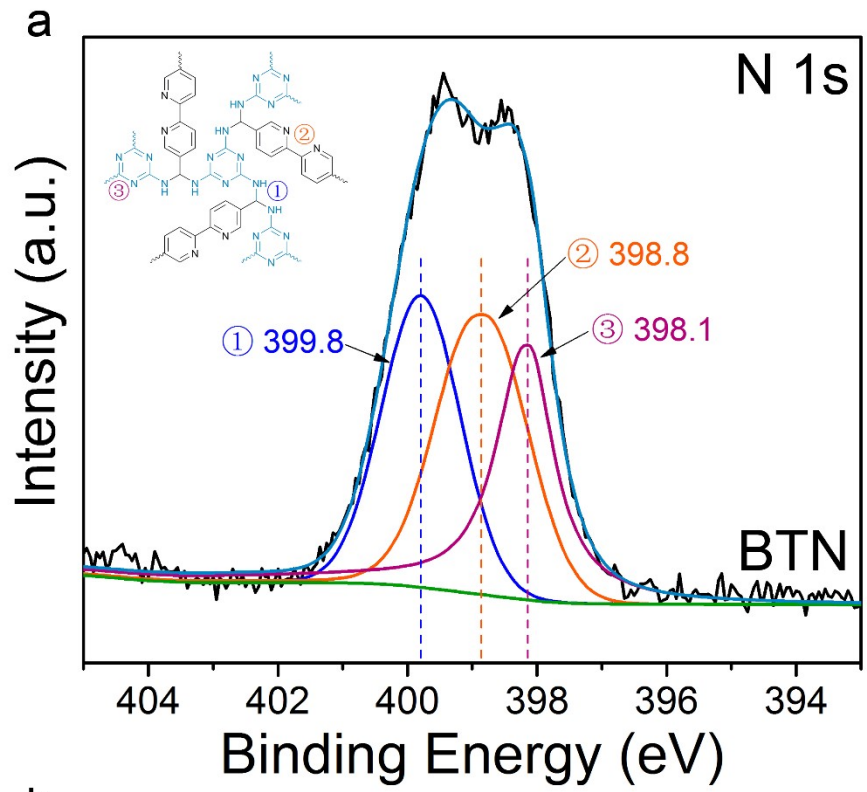
T : reaction time (8 h).

$\Omega[\text{Re}]$: actual content of Re (15.33%).

$M[\text{Re}]$: the relative atomic mass of Re (186.207 g/mol).



Scheme S1. Synthesis of BTN and BTN-Re. The inset are the samples.



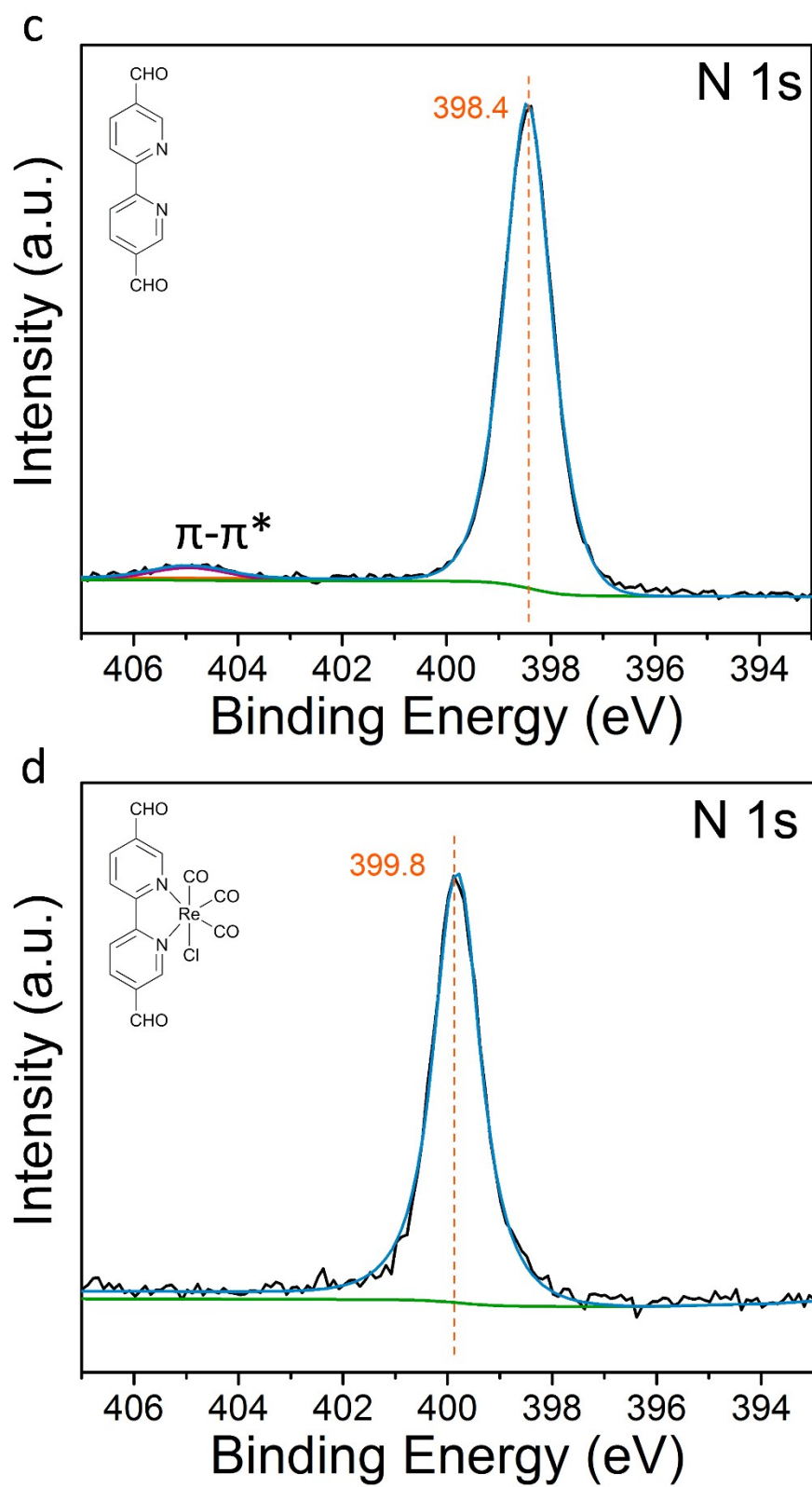


Fig. S1 XPS spectra of N 1s in (a) BTN; (b) BTN-Re; (c) 2,2'-Bipyridine-5,5'-dicarbaldehyde and (d) 2,2'-Bipyridine-5,5'-dicarbaldehydetricarbonylchlororhenium(I). The comparison of (c) and (d) shows that the N 1s binding energy will increase after coordination with Re.

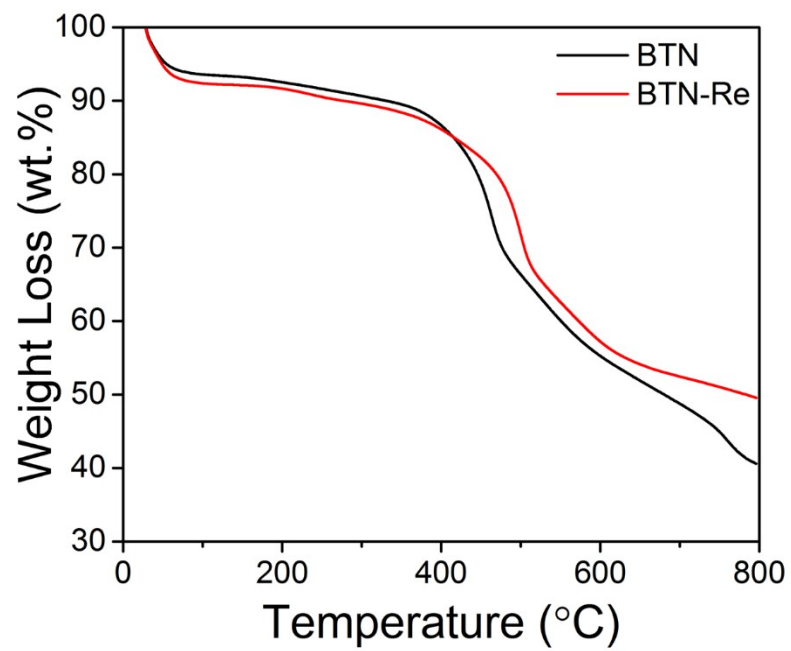


Fig. S2 TGA curves of BTN-Re and BTN analysed under N₂ atmosphere.

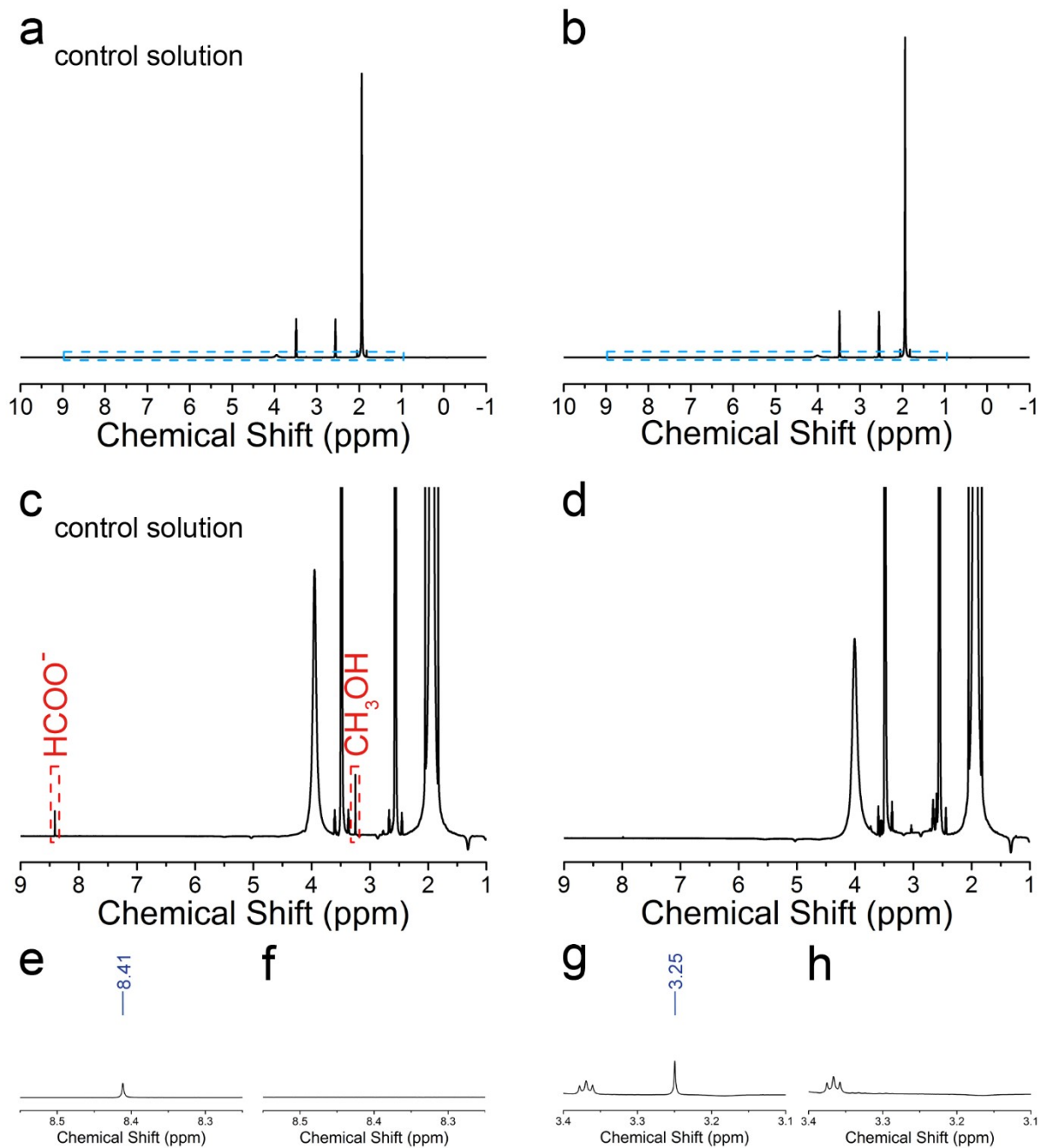


Fig. S3 (a-b) ^1H NMR spectrum of control solution and supernatant after photocatalytic reaction; (c-d) Corresponding partial enlargement. (Enlarged inside the blue dashed box); and (e-h) Finer comparisons near the chemical shift of formate ion and methanol.

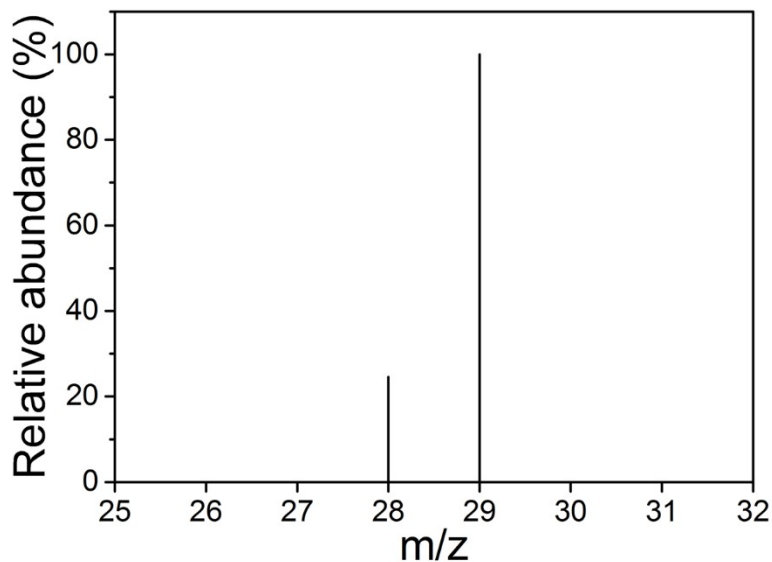


Fig. S4 Mass spectrum of CO obtained from the photocatalytic reaction.

Notes: Because the gas products were well separated by GC before entering the MS, both peaks at 28 and 29 are from CO. There may be two sources of ^{12}CO . One is the tiny amount of $^{12}\text{CO}_2$ in the reactant. The other is the carbonyl groups shed from BTN-Re, which is detected as CO. This can also prove that some carbonyl groups are detached from the catalyst after the photocatalytic reaction.

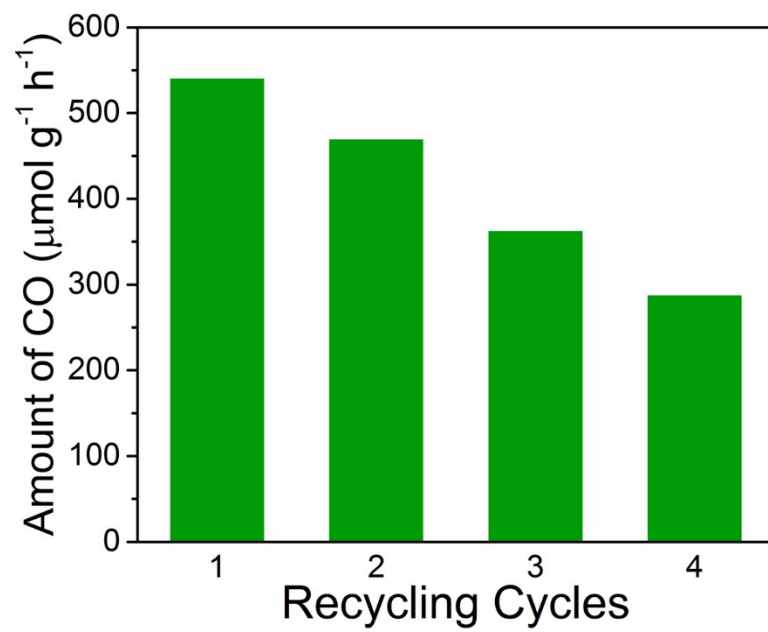


Fig. S5 The evolution of CO produced in four consecutive runs.

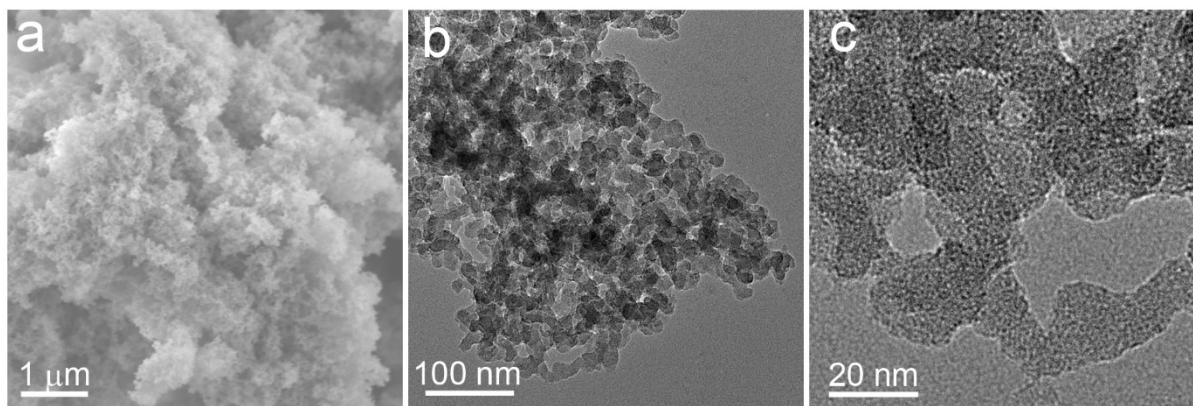


Fig. S6 (a) SEM and (b-c) TEM images of BTN-Re after photocatalytic reaction. There is no obvious change in the morphologies.

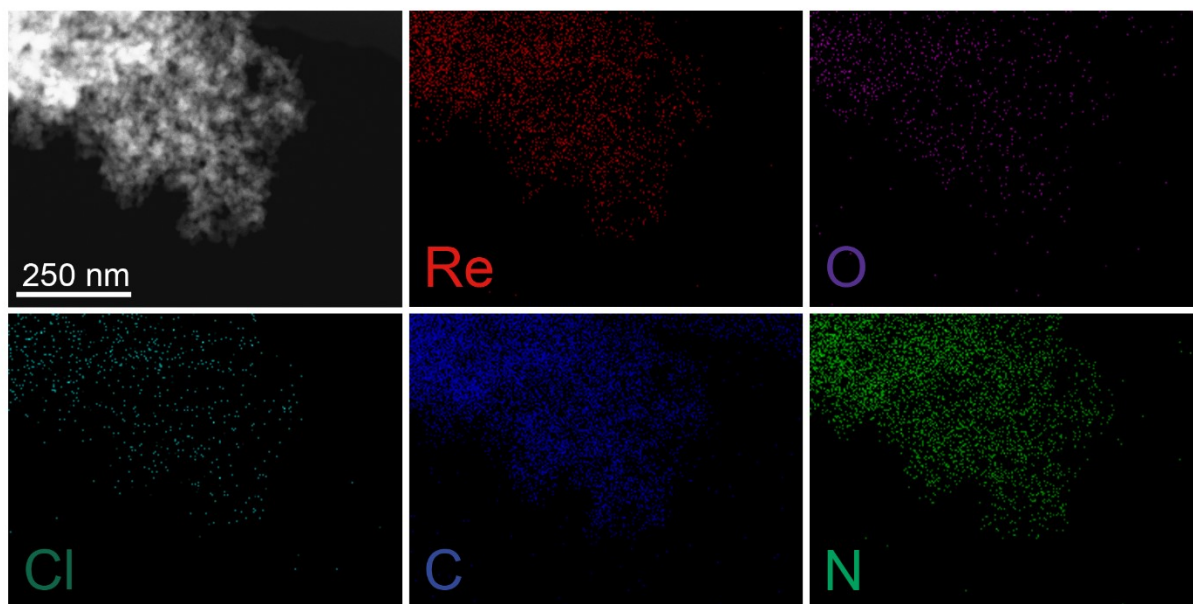


Fig. S7 EDS elemental mapping analysis of BTN-Re after photocatalytic reaction. Re, O, and Cl are still evenly distributed.

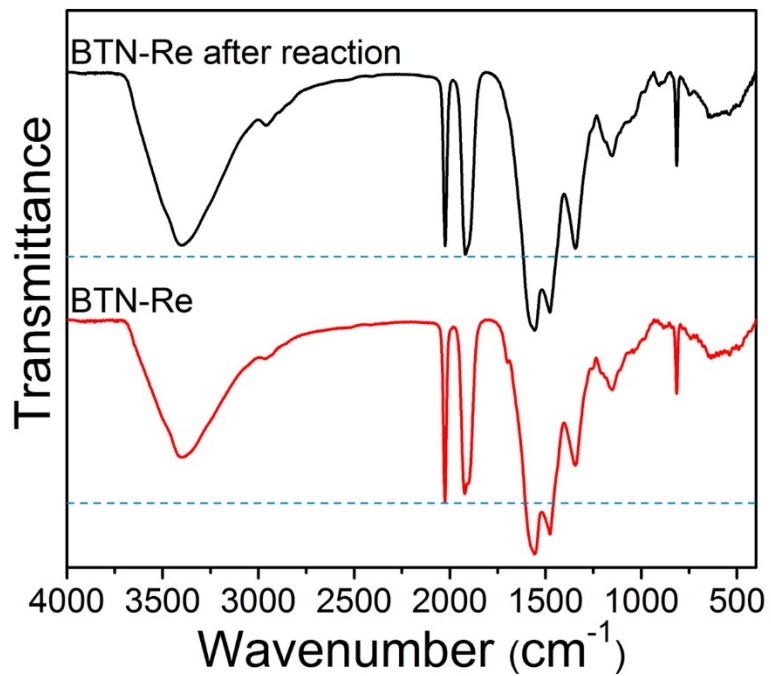


Fig. S8 FT-IR spectra of as-synthesized BTN-Re and BTN-Re after photocatalytic reaction. Intensities of the characteristic carbonyl bands ($2026, 1921$ and 1891 cm^{-1}) are decreased.

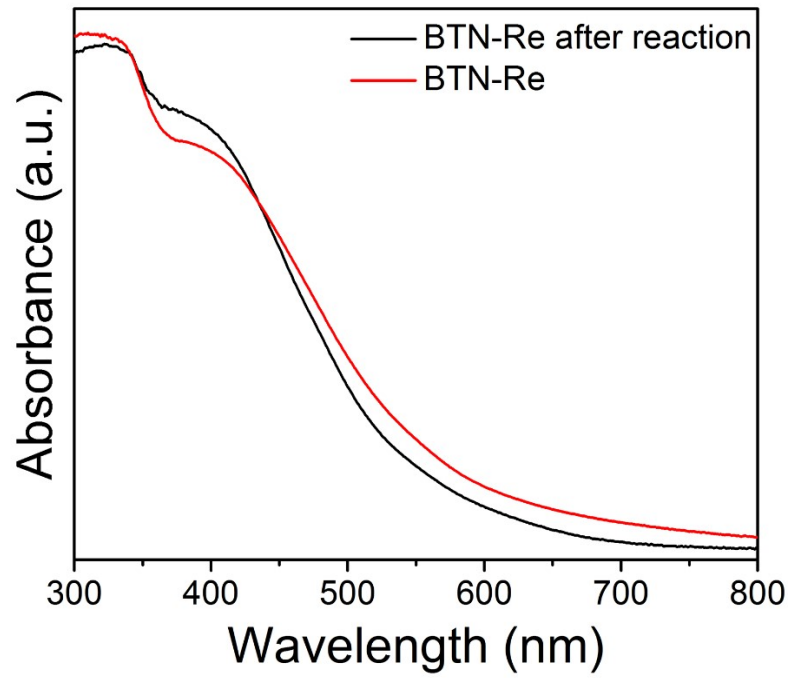


Fig. S9 UV/Vis DRS spectra of as-synthesized BTN-Re and BTN-Re after photocatalytic reaction.

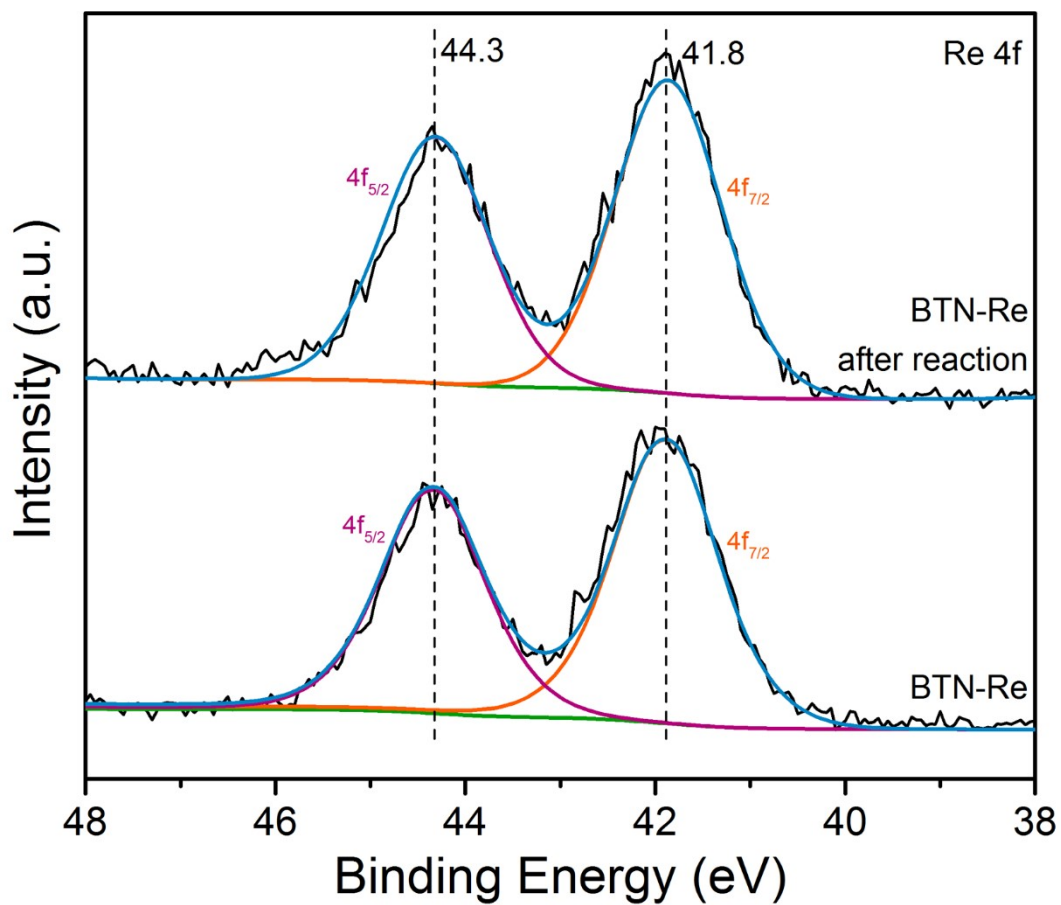


Fig. S10 XPS spectra of as-synthesized BTN-Re and BTN-Re after photocatalytic reaction. The chemical environment of Re has not changed significantly.

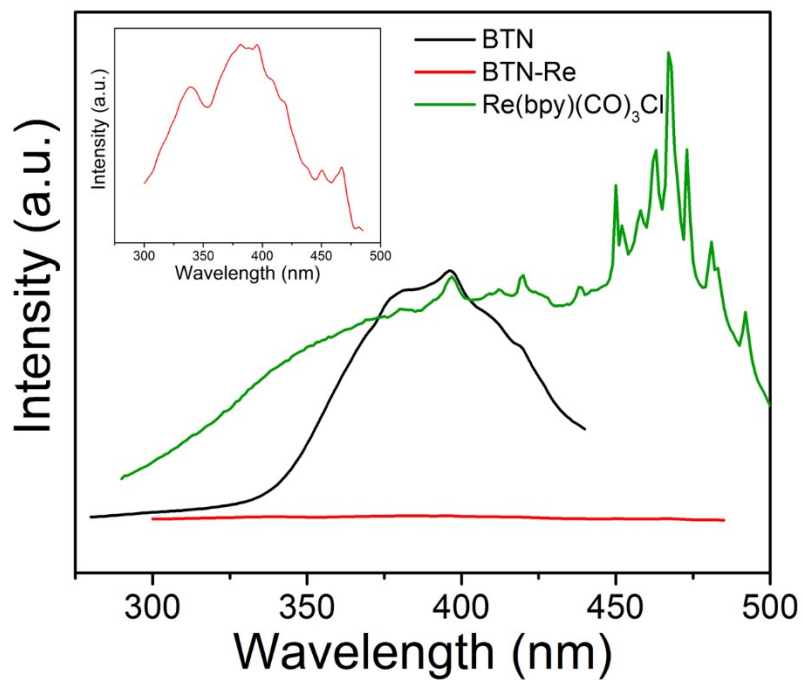


Fig. S11 PL excitation spectra of BTN, BTN-Re and Re(bpy)(CO)₃Cl. Inset: Clearer PL excitation spectrum of BTN-Re.

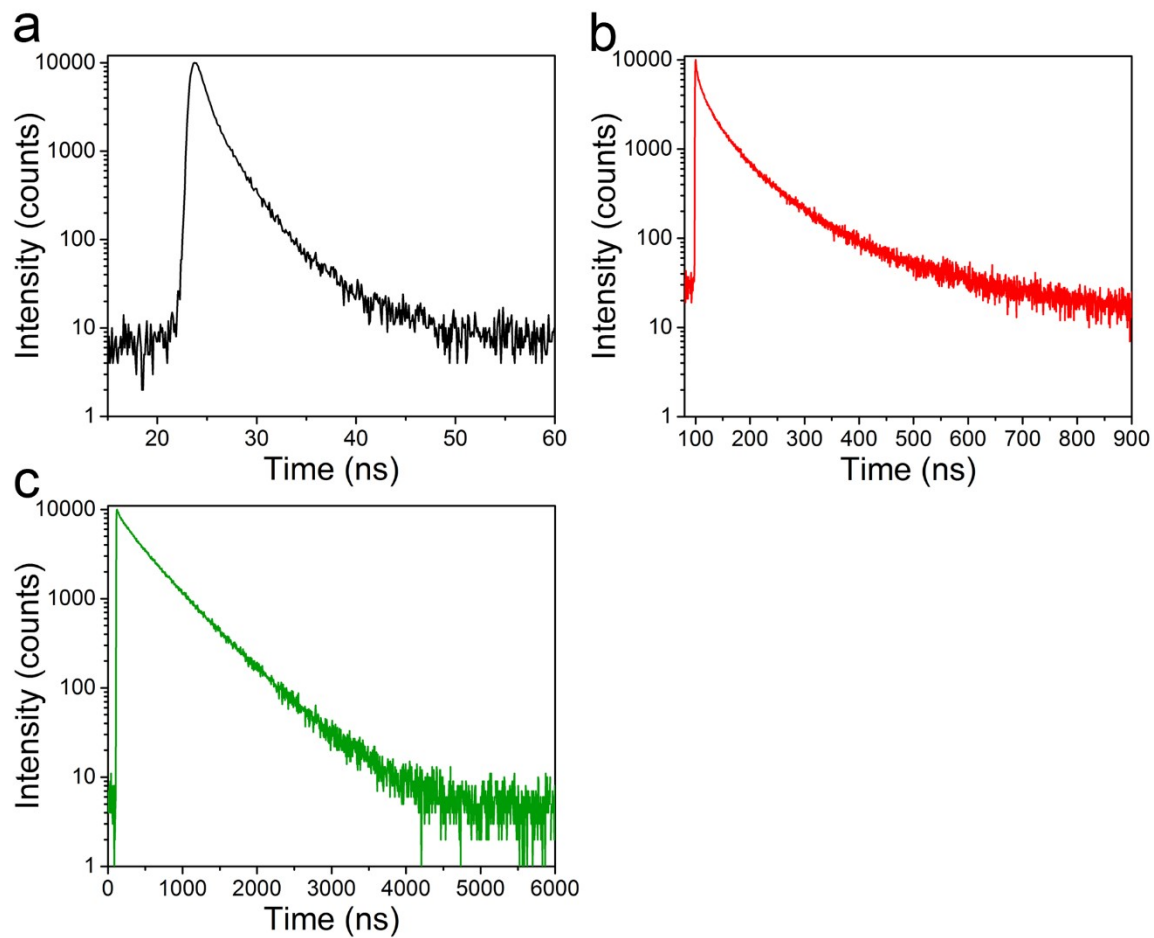


Fig. S12 Fluorescence decay curves of (a) BTN (excitation at 397 nm and emission at 495 nm); (b) BTN-Re (excitation at 397 nm and emission at 590 nm); and (c) Re(bpy)(CO)₃Cl (excitation at 400 nm and emission at 550 nm).

Control experiments	Change of corresponding conditions
No Catalyst	No catalyst was added
No Light	Wrap the reactor with aluminum foil
No TEOA	50 mL CH ₃ CN as reaction solution
No CO ₂	Argon instead of CO ₂ as reactant
BTN as a catalyst	10 mg BTN as a catalyst
Re(bpy)(CO) ₃ Cl as a catalyst	3.8 mg ^[a] Re(bpy)(CO) ₃ Cl as a catalyst
The mixture of Re(bpy)(CO) ₃ Cl and melamine as a catalyst	3.8 mg Re(bpy)(CO) ₃ Cl and 6.2 mg melamine as catalysts
24 hours experiment	The reaction time was extended to 24 hours, with a test every 2 hours

Table S1. The changed reaction conditions in the control experiments.

[a] The weight of Re(bpy)(CO)₃Cl is calculated based on the weight of BTN-Re and the Re content in BTN-Re.

Photocatalyst	Light source (nm)	Photosensitizer	Sacrificial agent	Solvent	Activity (CO) ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	reference
BTN-Re	400-780	/	TEOA	CH ₃ CN	500.7	This work
Re-COF	>420	/	TEOA	CH ₃ CN	~750	2
CPOP-30-Re	>390	/	TEOA	CH ₃ CN	623	4
Ag@Re ₃ MOF	400-700	/	TEA	CH ₃ CN	TON=0.014	5
Re-bpy-sp ² c-COF	>420	/	TEOA	CH ₃ CN	1040	6
	>420	(Ir[dF(CF ₃)ppy] ₂ (dtbpy))PF ₆	TEOA	CH ₃ CN	1400	
PCN-601	AM1.5G	/	H ₂ O	/	92 (CH ₄)	7
NNU-31-Zn	420-800	/	H ₂ O	H ₂ O	26.3	8
ZrPP-1-Co	>420	/	TEOA	CH ₃ CN	14	9
PEosinY-1	>420	/	H ₂ O	/	33	10

Table S2. Comparison of BTN-Re with Other Reported Heterogeneous Photocatalysts.

Sample	Maximum excitation wavelength λ_{ex} (nm)
BTN	397
BTN-Re	397
Re(bpy)(CO) ₃ Cl	468

Table S3. Maximum excitation wavelength of BTN, BTN-Re and Re(bpy)(CO)₃Cl.

Sample	Component	Lifetime (ns)	Intensity (%)	Decay Lifetime (ns)
BTN	τ_1	1.118	64.35	1.96
	τ_2	3.477	35.65	
BTN-Re	τ_1	7.621	10.97	67.71
	τ_2	39.66	54.13	
Re(bpy)(CO) ₃ Cl	τ_3	130.1	34.9	468.7
	τ_1	227.1	22.24	
	τ_2	537.8	77.76	

Table S4. Fitted parameters of time-resolved PL spectra

References

- 1 E. M. Johnson, R. Haiges and S. C. Marinescu, *ACS Appl. Mater. Interfaces*, 2018, 10, 37919-37927.
- 2 S. Yang, W. Hu, X. Zhang, P. He, B. Pattengale, C. Liu, M. Cendejas, I. Hermans, X. Zhang, J. Zhang and J. Huang, *J. Am. Chem. Soc.*, 2018, 140, 14614-14618.
- 3 W. Zhang, Q. Qin, L. Dai, R. Qin, X. Zhao, X. Chen, D. Ou, J. Chen, T. T. Chuong, B. Wu and N. Zheng, *Angew. Chem., Int. Ed.*, 2018, 57, 9475-9479.
- 4 H.-P. Liang, A. Acharjya, D. A. Anito, S. Vogl, T.-X. Wang, A. Thomas and B.-H. Han, *ACS Catal.*, 2019, 9, 3959-3968.
- 5 K. M. Choi, D. Kim, B. Rungtaweeworant, C. A. Trickett, J. T. Barmanbek, A. S. Alshammari, P. Yang and O. M. Yaghi, *J. Am. Chem. Soc.*, 2017, 139, 356-362.
- 6 Z. Fu, X. Wang, A. M. Gardner, X. Wang, S. Y. Chong, G. Neri, A. J. Cowan, L. Liu, X. Li, A. Vogel, R. Clowes, M. Bilton, L. Chen, R. S. Sprick and A. I. Cooper, *Chem. Sci.*, 2020, 11, 543-550.
- 7 Z.-B. Fang, T.-T. Liu, J. Liu, S. Jin, X.-P. Wu, X.-Q. Gong, K. Wang, Q. Yin, T.-F. Liu, R. Cao and H.-C. Zhou, *J. Am. Chem. Soc.*, 2020, 142, 12515-12523.
- 8 L.-Z. Dong, L. Zhang, J. Liu, Q. Huang, M. Lu, W.-X. Ji and Y.-Q. Lan, *Angew. Chem., Int. Ed.*, 2020, 59, 2659-2663.
- 9 E.-X. Chen, M. Qiu, Y.-F. Zhang, Y.-S. Zhu, L.-Y. Liu, Y.-Y. Sun, X. Bu, J. Zhang and Q. Lin, *Adv. Mater.*, 2018, 30, 1704388.
- 10 X. Yu, Z. Yang, B. Qiu, S. Guo, P. Yang, B. Yu, H. Zhang, Y. Zhao, X. Yang, B. Han and Z. Liu, *Angew. Chem., Int. Ed.*, 2019, 58, 632-636.