

A Cu(I) based Boron Imidazolate Framework for Visible-Light Driven CO₂ Reduction

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Experiment section

Materials and methods. All chemical reagents for syntheses were used as purchased without further purification. All the solvents used were analytical reagent, 99%. The photosensitizer ([Ru(bpy)₃]Cl₂·6H₂O) was purchased from Damas-beta company. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer (MiniFlex-II) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of 5–50° with a scanning rate of 5° min⁻¹. Thermogravimetric analysis (TGA) was performed on a NETSCHZ STA-449C thermoanalyzer in N₂ with a heating rate of 10 °C min⁻¹ from 25 to 800 °C. A UV-visible spectrophotometer (Lambda 950, PerkinElmer) was used to measure the absorption spectra of the as-prepared samples with BaSO₄ as a standard (100% reflectance). The Fourier transform infrared spectroscopy (FT-IR) data (KBr pellets) was recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer.

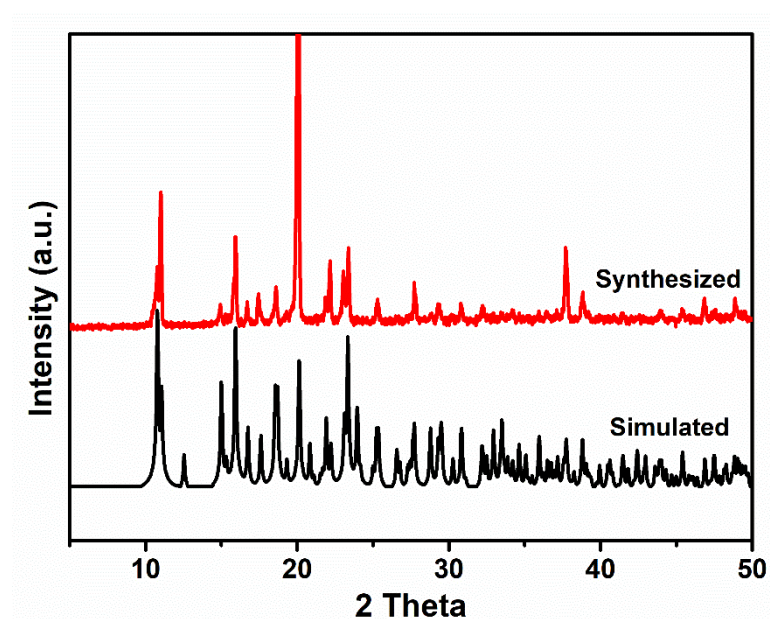
Synthesis of KBH(im)₃ ligands. The KBH(im)₃ ligands were synthesized based on a reported procedure with a slight modification.¹⁻³ The reaction was carried out in a flask filled with nitrogen. KBH₄ (1.08 g, 20.0 mmol) and imidazole (4.16 g, 61.2 mmol) were mixed and heated to 195°C under stirring. During the heating process, the mixed solids were melted, and hydrogen gases were generated. About 30 min, the evolution of gas ceased. Then cooled to room temperature, the product KBH(im)₃ was obtained as off-white solid.

Synthesis of BIF-105 crystals. KBH(im)₃ (40.0 mg, 0.158 mmol), glutaric acid (27.0 mg, 0.204 mmol) and CuCl₂·2H₂O (136 mg, 0.798 mmol) were mixed in deionized water (1 mL)/methyl alcohol (1 mL)/3-amino propanol (4 mL) solution in a 20 mL vial and stirred for about ten minutes. The mixture was heated at 80 °C for 4 days, followed by cooling to room temperature. The light yellow crystals were obtained. Yield, 42% based on B.

Photocatalytic CO₂ reduction experiments. The photocatalytic reduction of CO₂ was carried out in a 400 mL reactor and irradiated under a 300-W (PLS-SXE300D) Xe lamp with a 420 nm cutoff filter. Prior to light illumination, the whole reaction setup was vacuumed and then the high purity CO₂ gas was bubbled into the reaction setup to reach a pressure of 1 atm. In a typical reaction system, the catalyst BIF-105 (10.0 mg, 36.2 μmol based on copper) was suspended in acetonitrile/H₂O (v/v = 4:1) containing 5% (v/v) TEOA (90 mL, pH = 9.3 adjusted with 60.0 μL HNO₃ and tested by PH meter (PHS-3C)) and [Ru(bpy)₃]Cl₂·6 H₂O (75.0 mg), by stirring with a magnetic stirrer. The generated gas products were analyzed by a gas chromatography analyzer (FULI 9790II) equipped with the flame ionization detector (FID, TDX-01 packed column) and thermal conductivity detector (TCD, 5Å LSX packed column). The flow rates of hydrogen and air are 45 mL/min and 300 mL/min, respectively. And the argon acts as carrier gas, with the flow rate of 30 mL/min. Each reaction was repeated three times to ensure the reliability of the experiment data.

Table S1. Summary of crystal data and structural refinements for BIF-105

Compound reference	BIF-105
Chemical formula	Cu(BH(im) ₃)
Chemical formula sum	CuC ₉ H ₁₀ BN ₆
Formula mass	276.58
Crystal system	monoclinic
a [Å]	8.014(6)
b [Å]	14.104(10)
c [Å]	10.095(8)
α [°]	90.00
β [°]	94.207(11)
γ [°]	90.00
Unit cell volume [Å ³]	1138.1(15)
Temperature [K]	293(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>
No. of formula units per unit cell, Z	4
No. of reflections measured	7934
No. of independent reflections	2401
<i>R</i> _{int}	0.0502
Final R1 values (I > 2σ(I))	0.0379
Final wR(F ²) values (I > 2σ(I))	0.1201
Goodness of fit on F ²	1.087

**Figure S1.** The Powder XRD patterns of BIF-105 (simulated and synthesized).

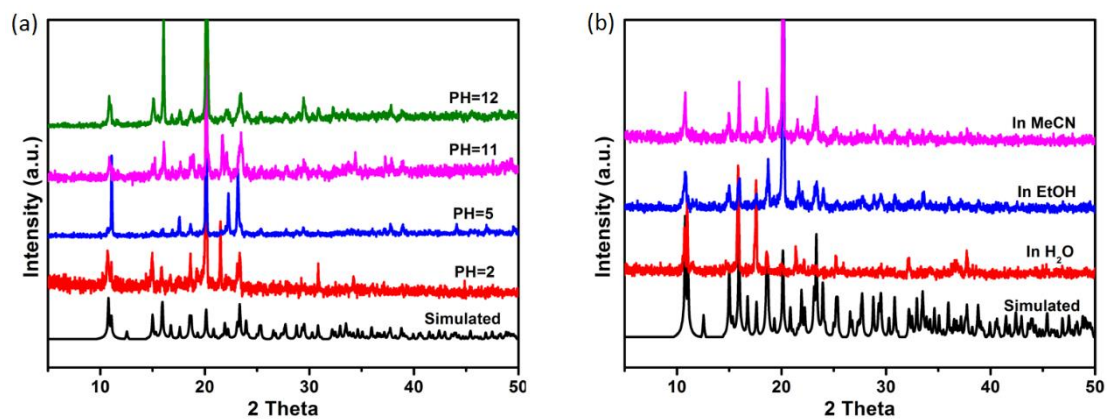


Figure S2. (a) The Powder XRD patterns of BIF-105 (simulated, immersed in pH = 2, 5, 11, 12 aqueous). (b) The Powder XRD patterns of BIF-105 (simulated, immersed in H₂O, EtOH, MeCN).

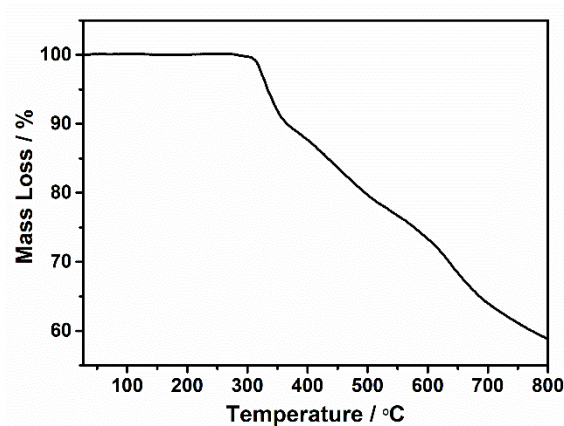


Figure S3. The TGA plot of BIF-105.

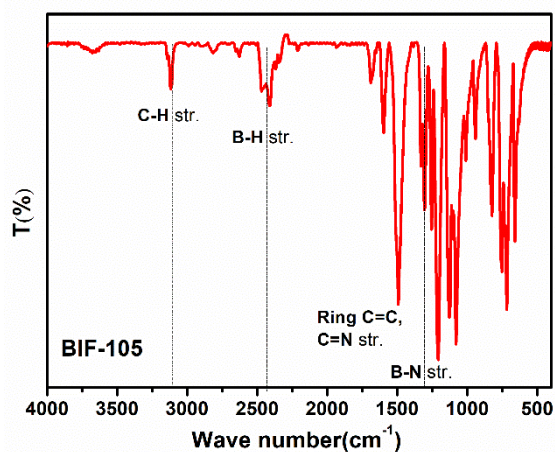


Figure S4. FT-IR analysis of BIF-105.

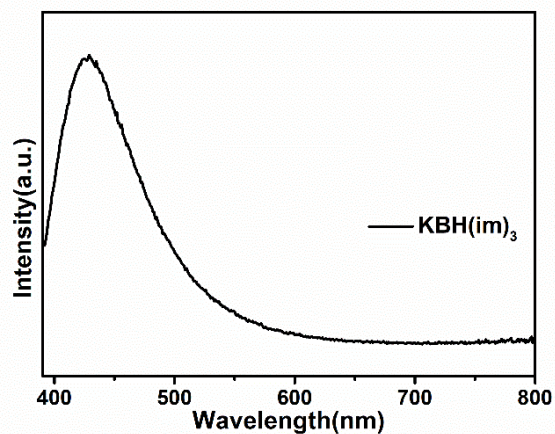


Figure S5. The emission wavelength of $\text{KBH}(\text{im})_3$ ($\lambda_{\text{ex}}=375\text{nm}$).

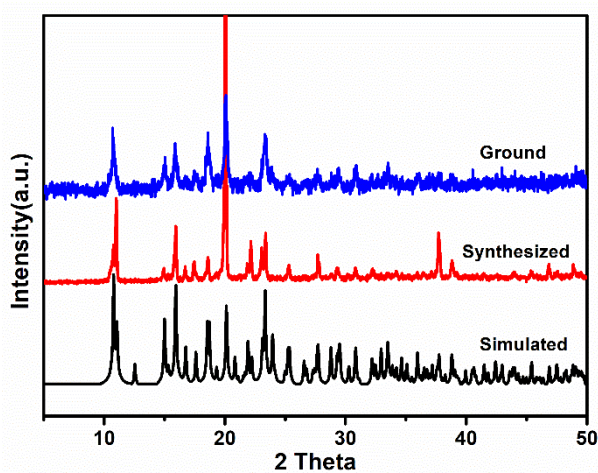


Figure S6. The Powder XRD patterns of BIF-105 and its ground sample.

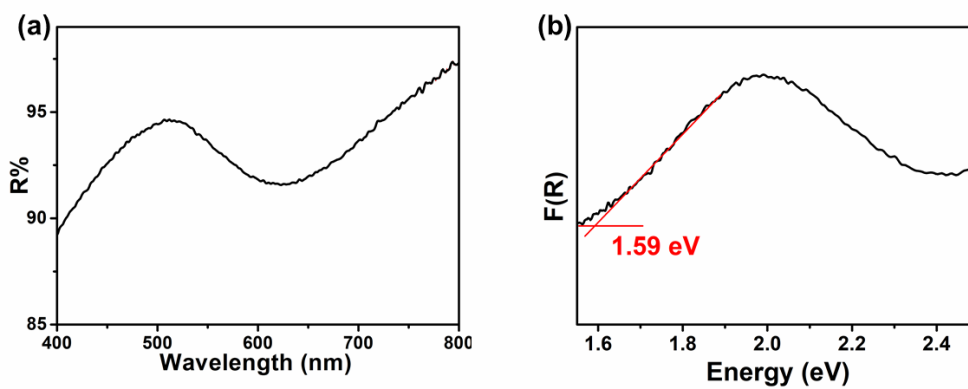


Figure S7. (a) The UV-Vis diffusion spectrum of BIF-105. (b) Tauc plots of BIF-105 for band gap calculation based on UV-Vis spectrum.

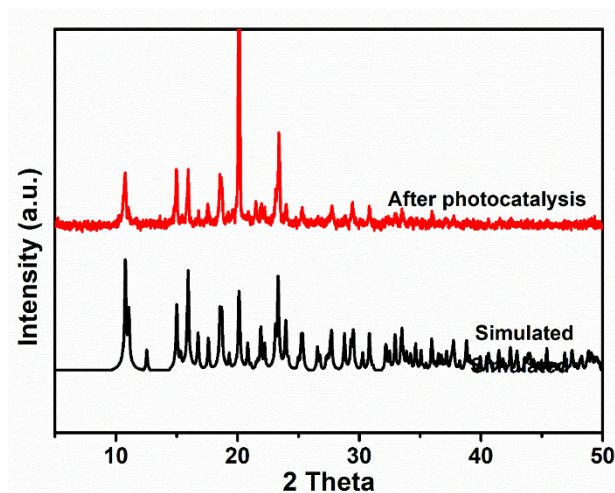


Figure S8. The Powder XRD patterns of BIF-105 and the crystals after 6-hour photocatalysis.

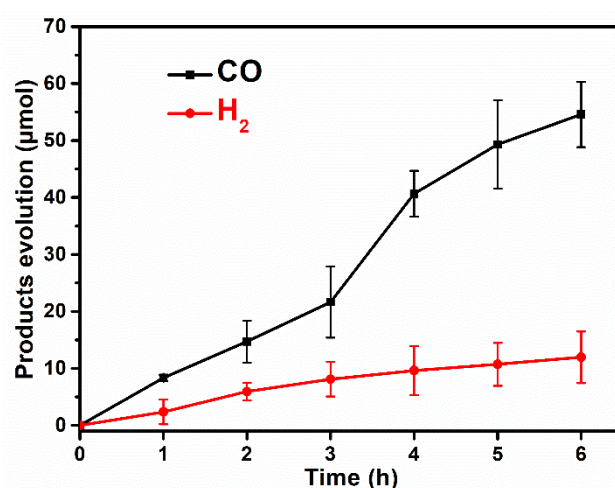


Figure S9. The parallel experiments. Experiment conditions: 90mL CH₃CN/H₂O (v/v = 4:1) solution with 5% TEOA, PH=9.3, 75 mg [Ru(bpy)₃]Cl₂.

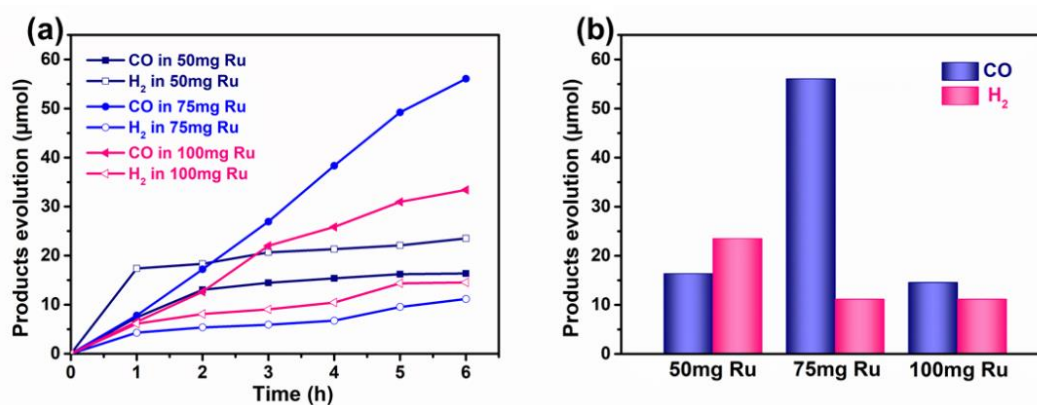


Figure S10. The variable concentration studies of the Ru-based photosensitizer [Ru(bpy)₃]Cl₂·6 H₂O. Experiment conditions: 90mL CH₃CN/H₂O (v/v = 4:1) solution with 5% TEOA, PH=9.3.

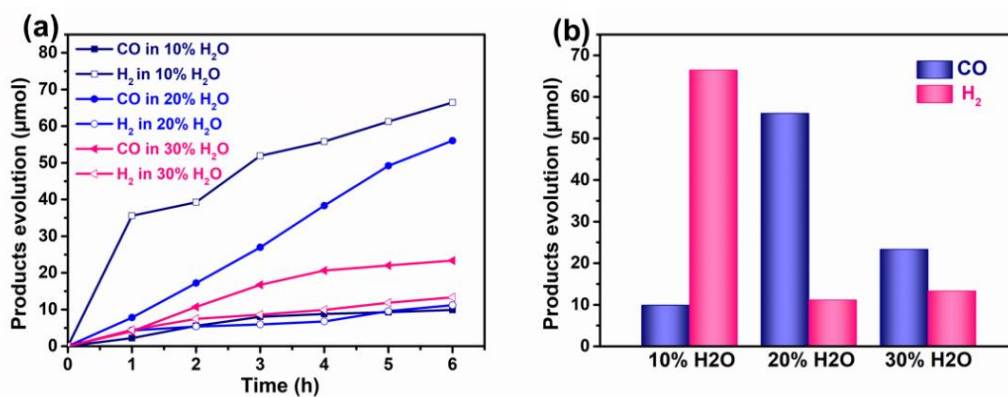


Figure S11. The relative concentration of water. Experiment conditions: 90mL solution with 5% TEOA, PH=9.3, 75 mg [Ru(bpy)₃]Cl₂.

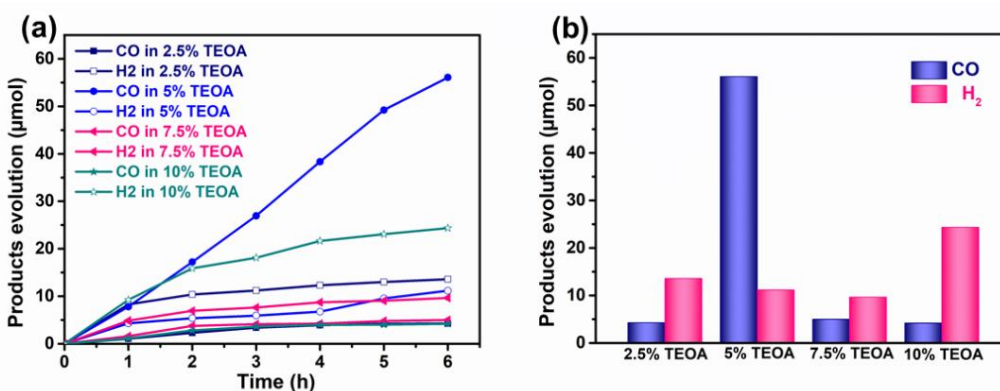


Figure S12. The relative concentration of TEOA. Experiment conditions: 90mL CH₃CN/H₂O (v/v = 4:1) solution, PH=9.3, 75 mg [Ru(bpy)₃]Cl₂.

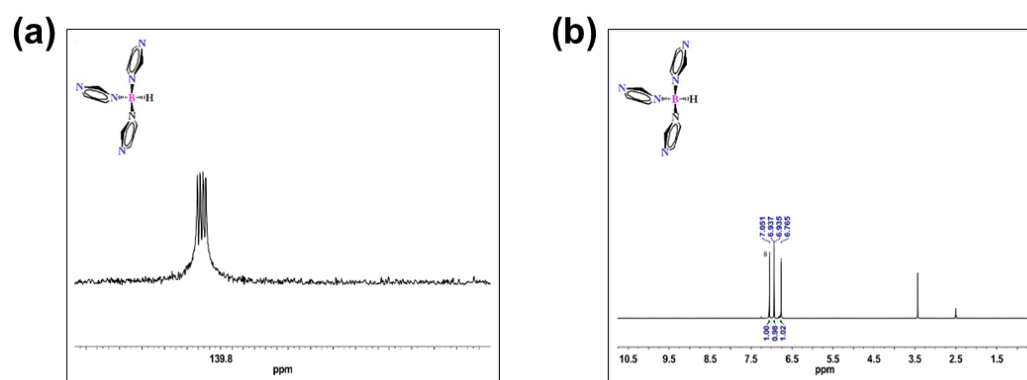


Figure S13. The NMR spectra of KBH(im)₃ ligand in DMSO-*d*₆, carbon (a) and ¹H (b).

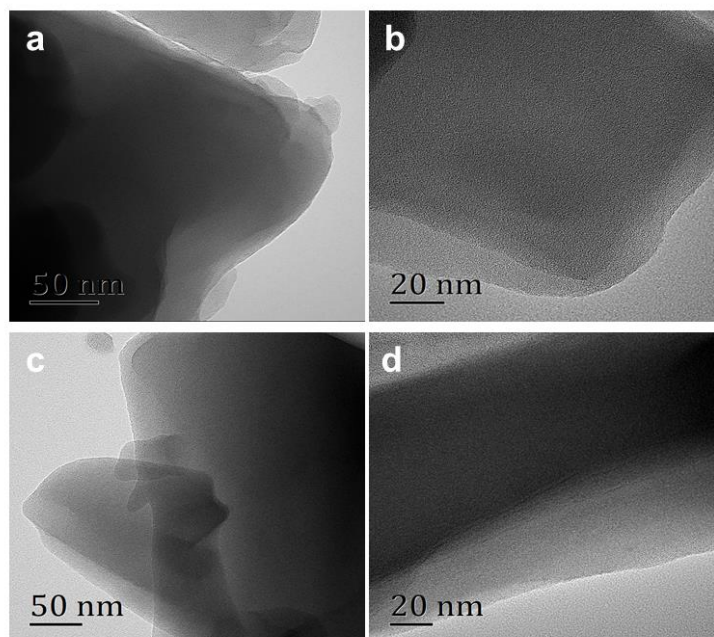
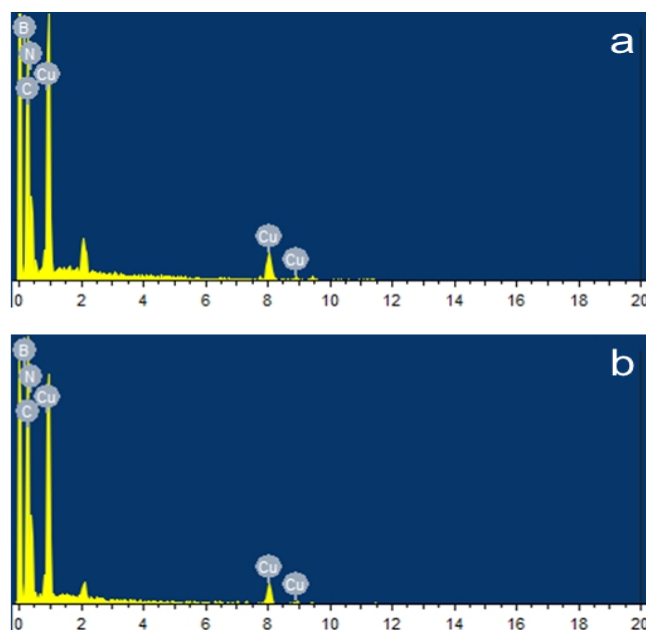


Figure S14. The Transmission Electron Microscope patterns of as-synthesized BIF-105 (a and b) and the crystals after 6-hour photocatalysis (c and d).



Element	BIF-105		BIF-105 after photocatalysis	
	Mass percent	Atomic percent	Mass percent	Atomic percent
B	18.17	24.18	14.62	19.56
C	38.93	46.62	40.20	48.38
N	24.34	25.00	27.08	27.95
Cu	18.55	4.20	18.10	4.12

Figure S15. The EDX patterns of BIF-105 (a) and the crystals after 6-hour photocatalysis (b).

Table S2. Performance comparison of our sample with state-of-the-art catalysts for CO₂ photoreduction.

Catalyst (used amount)	Photosensitizer	Electron donor	Solvent	Light source (nm)	Major Product rate ^a	Ref.
BIF-105	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	TEOA	MeCN/H ₂ O	λ > 400 (Xe lamp)	CO 933 μmol·g ⁻¹ ·h ⁻¹	This work
PCN-222	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	HCOO ⁻ 60	<i>J. Am. Chem. Soc.</i> 2015, 137 , 13440.
ZrPP-1-Co	/	TEOA	MeCN	λ>420 (Xe lamp)	CO 14.0 μmol·h ⁻¹	<i>Adv. Mater.</i> 2018, 30 , 1704388.
Hf ₁₂ -Ru-Re	/	BNAH or BIH	MeCN	λ > 400 (Xe lamp)	CO (TON) 3849 (BIH) or 2092 (BNAH)	<i>J. Am. Chem. Soc.</i> 2018, 140 , 12369–12373
Co-ZIF-9	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	TEOA	MeCN/H ₂ O	λ>420 (Xe lamp)	CO 83.6 μmol·h ⁻¹	<i>Angew. Chem. Int. Ed.</i> 2014, 53 , 1034.
ZIF-67	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	TEOA	MeCN/H ₂ O	λ>420 (Xe lamp)	~14.0 μmol·g ⁻¹ ·h ⁻¹	<i>Appl. Catal. B</i> 2017, 209 , 476.
NH ₂ -MIL-125(Ti)	/	TEOA	MeCN	λ>420 (Xe lamp)	HCOO ⁻ 16.3 mmol·h ⁻¹ ·g ⁻¹	<i>Angew. Chem. Int. Ed.</i> 2012, 51 , 3364.
Zn ₂ GeO ₄ / Mg-MOF-74	/	H ₂ O	MeCN/H ₂ O	200-1100 (Xe lamp)	CO ~1.44 μmol·g ⁻¹ ·h ⁻¹	<i>Catal. Sci. and Technol.</i> 2018, 8 , 1288.
BIF-29	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	TEOA	MeCN / H ₂ O	λ>420 (Xe lamp)	3334 μmol g ⁻¹ h ⁻¹	<i>Angew. Chem. Int. Ed.</i> 2019, 58 , 11752.

References

1. B. H. Hamilton, K. A. Kelly, W. Malasi and C. J. Ziegler, *Inorg. Chem.* 2003, **42**, 3067-3073.
2. Trofimenko, S. *J. Am. Chem. Soc.* 1967, **89**, 3170-3177.
3. Trofimenko, S. *J. Coord. Chem.* 1972, **2**, 75-77.