Supporting Information

Highly Efficient Photocatalytic CO_2 Reduction by a Ruthenium Complex Sensitizing g-C_3N_4/MOF Hybrid Photocatalyst

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Experimental section

Materials

Chemical reagents were purchased from Aladdin or Sigma-Aldrich and used without further purification: $RuCl_3 \cdot 3H_2O$, LiCl, $Co(NO_3)_2 \cdot 6H_2O$, $RuCl_3 \cdot 3H_2O$, 2,2-bipyridyl (bpy), KPF_6, urea, $NaHCO_3$, 2,5-Dihydroxyterephthalic acid (H_4DOBDC), 2,2'-bipyridyl-4,4'-dicarboxylic acid (H_2dcbpy), Tetrabutylammonium hexafluorophosphate (NBu_4PF_6), ethanol, methanol, acetic acid, deionized water, acetonitrile (MeCN), N,N-dimethylformaide (DMF), and triethanolamine (TEOA).

Preparation of ruthenium complexes (RuL_2L')

The $[Ru^{II}(bpy)_2(H_2dcbpy)](PF_6)_2$ complex was synthesized according to the reported[1].

Synthesis of exfoliated g-C_3N_4

The exfoliated g-C_3N_4 was prepared according to the literature[2].

Preparation of g-C_3N_4/MOF

Different amount g-C_3N_4 samples (100 mg, 200 mg and 400 mg) were ultrasound treated in 10 mL DMF for 30 min. And the solid mixture of H_4DOBDC (40 mg, 0.2 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (233 mg, 0.8 mmol) were dissolved in a 20 mL solution that consisted of DMF, water and EtOH at a volume ratio of 2:1:1, which was ultrasound to form a homogeneous solution. Then the solution of g-C_3N_4 was added slowly to the mixed solution under ultrasound. Subsequently, the mixed solution was

transferred into 50 mL Telflonlined autoclave and treated in an oven at 120 °C for 24 h. The resultant suspension was filtered and washed with H_2O, DMF, and EtOH and finally dried at 100 °C for 6 h in a vacuum desiccator.

Preparation of $RuL_2L'@C_3N_4$/MOF

The g-C_3N_4/MOF complex was dispersed in 20 mL DMF, the same amount of RuL_2L' as g-C_3N_4 added into the solution (Table. S1). The suspension was stirred at room temperature in the dark overnight[3]. Here, the obtained samples $RuL_2L'@xC_3N_4$/MOF containing 100, 200 and 400 mg C_3N_4 named $RuL_2L'@100C_3N_4$/MOF, $RuL_2L'@200C_3N_4$/MOF and $RuL_2L'@400C_3N_4$/MOF, respectively.

Characterizations

Crystal phase structures were conducted via a powder X-ray diffraction (XRD, SmartLab 9KW), the morphology and microstructure of all samples were analyzed by scanning electron microscopy (SEM, Bruker Smart APEX II) and transmission electron microscopy (TEM, Tecnai G2 F30). The chemical states on the surface of photocatalysis were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB XI+). The photoluminescence (PL) spectra were recorded on the steady-state spectrophotometer (HORIBA Jobin Yvon FluoroMax-4). Solid-state UV–vis diffuse absorption spectra were obtained with Lambda 750S spectrophotometer. The infrared spectra were obtained using a Fourier transform infrared (FT-IR) spectrometer (Bruker VERTEX 80v).

Photocatalytic Performance Test

Typically, a mixture of 1 mg $RuL_2L'@C_3N_4$/MOF, 1 mg bpy, proper amount of TEOA as electronic donor and 4 mL MeCN was placed in the Schlenk cube (25 mL). And the mixture degassed by CO_2 for half an hour. After the CO_2 was saturated, the solution was irradiated by the 300W Xe almp equipped with a 400 nm cutoff filter. The generated gas was analyzed by gas chromatograph (GC-7900) every half hour.

Mott-Schottky, transient photocurrent responses and electrochemical impedance spectroscopy (EIS)

The sample (3 mg) was dissolved in 1 mL H_2O/EtOH = 3:1 and ultrasound for 30 minutes. Then 80 μL nafion added in the mixture solution and ultrasound for 30 minutes. The preparation for working electrode was that 0.1 mL slurry was dropped onto FTO and dried at 40 °C for 10 minutes. The solution purged with Ar before

electrochemistry test. The reference electrode and counter electrode were Ag/AgCl electrode and Pt electrode, respectively. A solution of 0.5 M Na_2SO_4 served as electrolyte solution for Mott-Schottky, transient photocurrent responses and EIS measurements.

Cyclic Voltammogram (CV) tests

1 mM RuL_2L' was dissolved in 30 mL CH_3CN with 0.1 M NBu_4PF_6. CV was tested in a standard three-electrode cell. The reference electrode, counter electrode and working electrode were saturated $Ag/AgNO_3$, Pt electrode and glassy carbon electrode, respectively.

References

1. P. Pearson, A. M. Bond, G. B. Deacon, C. Forsyth and L. Spiccia, *Inorg. Chim. Acta*, 2008, **361**, 601-612.

2. J. Xu, L. Zhang, R. Shi and Y. Zhu, *J. of Mat. Chem. A, Mat. for En. and Sustain.*, 2013, **1**, 14766.

3. R. Kuriki, M. Yamamoto, K. Higuchi, Y. Yamamoto, M. Akatsuka, D. Lu, S. Yagi, T. Yoshida, O. Ishitani and K. Maeda, *Angew. Chem. Int. Ed. Engl*, 2017, **56**, 4867-4871.

Tab. S1. Synthesis of different content of $RuL_2L'@xC_3N_4$/MOF

number	g-C_3N_4	RuL_2L'	Co^{2+}	H_4DOBDC	named
1	100 mg	100 mg	233 mg	40 mg	$RuL_2L'@100C_3N_4$-MOF
2	200 mg	200 mg	233 mg	40 mg	$RuL_2L'@200C_3N_4$-MOF
4	400 mg	400 mg	233 mg	40 mg	$RuL_2L'@400C_3N_4$-MOF

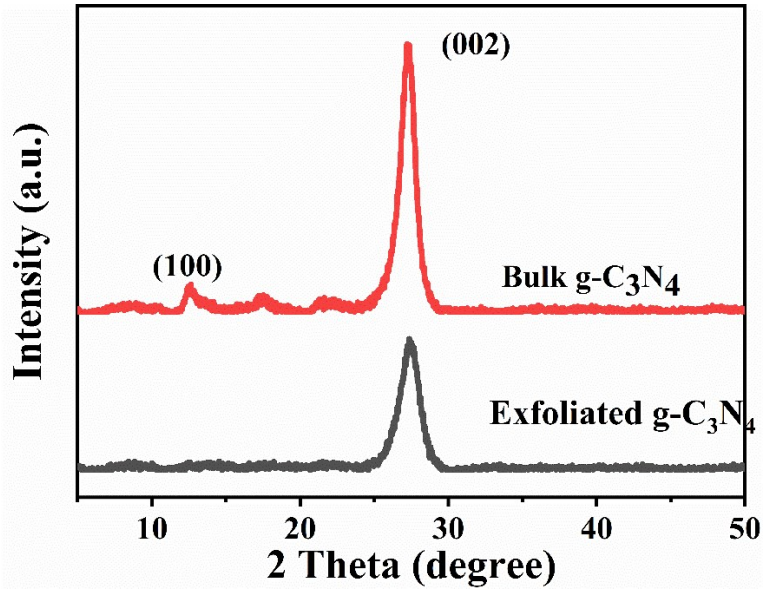

Fig. S1. XRD of bulk g-C_3N_4 and exfoliated g-C_3N_4.

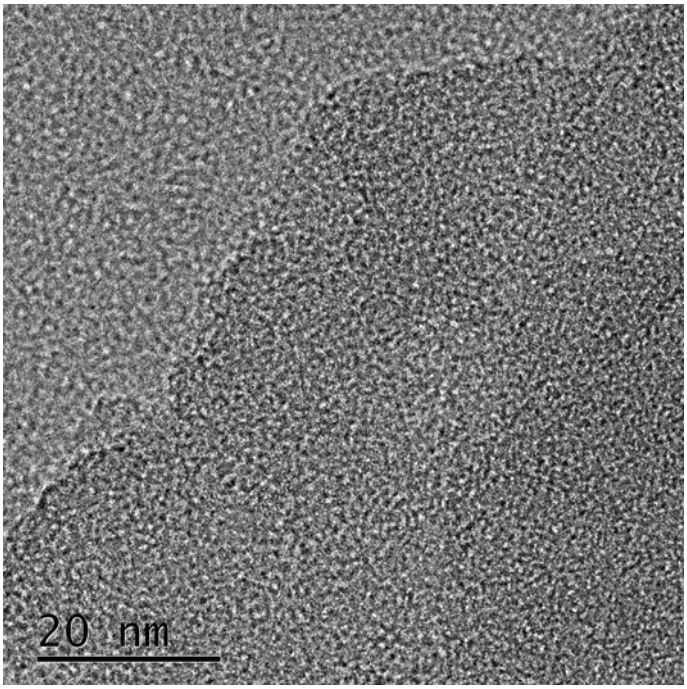

Fig. S2. TEM image of exfoliated g-C_3N_4.

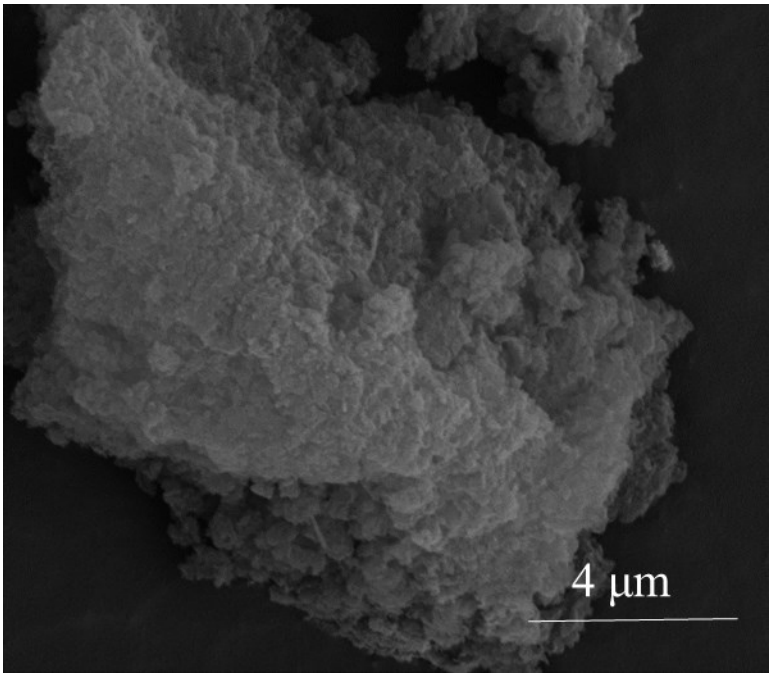

Fig. S3. SEM image of exfoliated g-C_3N_4.

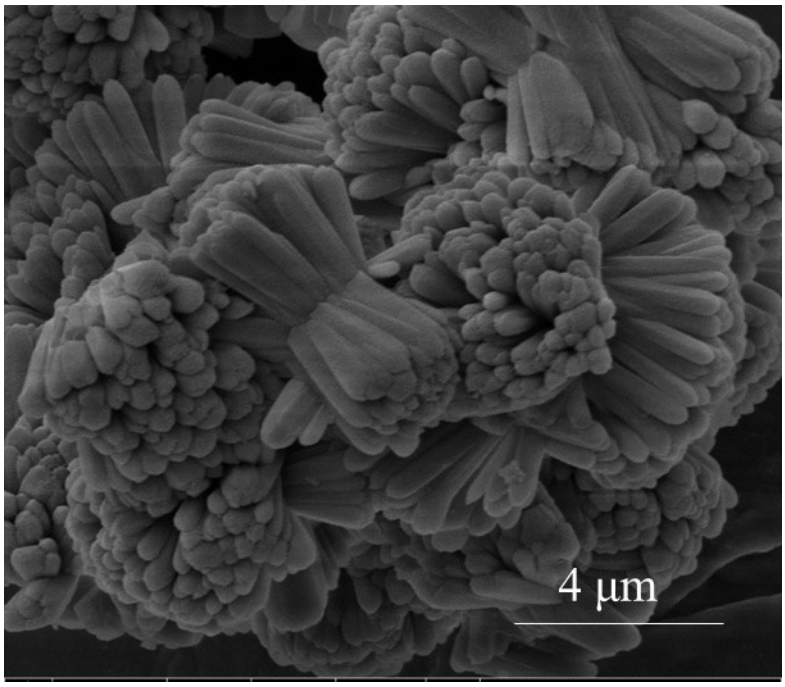

Fig. S4. SEM image of Co-MOF-74.

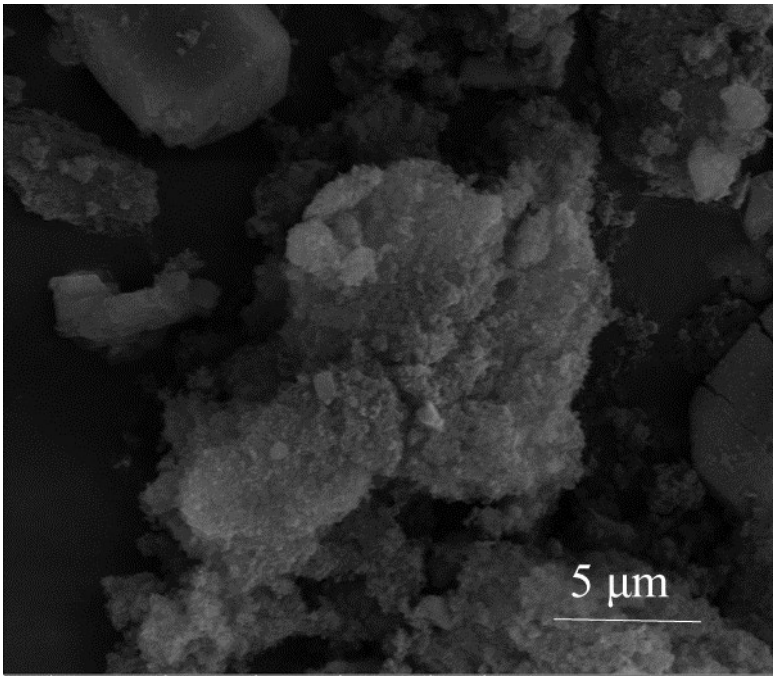

Fig. S5. SEM image of $RuL_2L'@200C_3N_4/MOF$

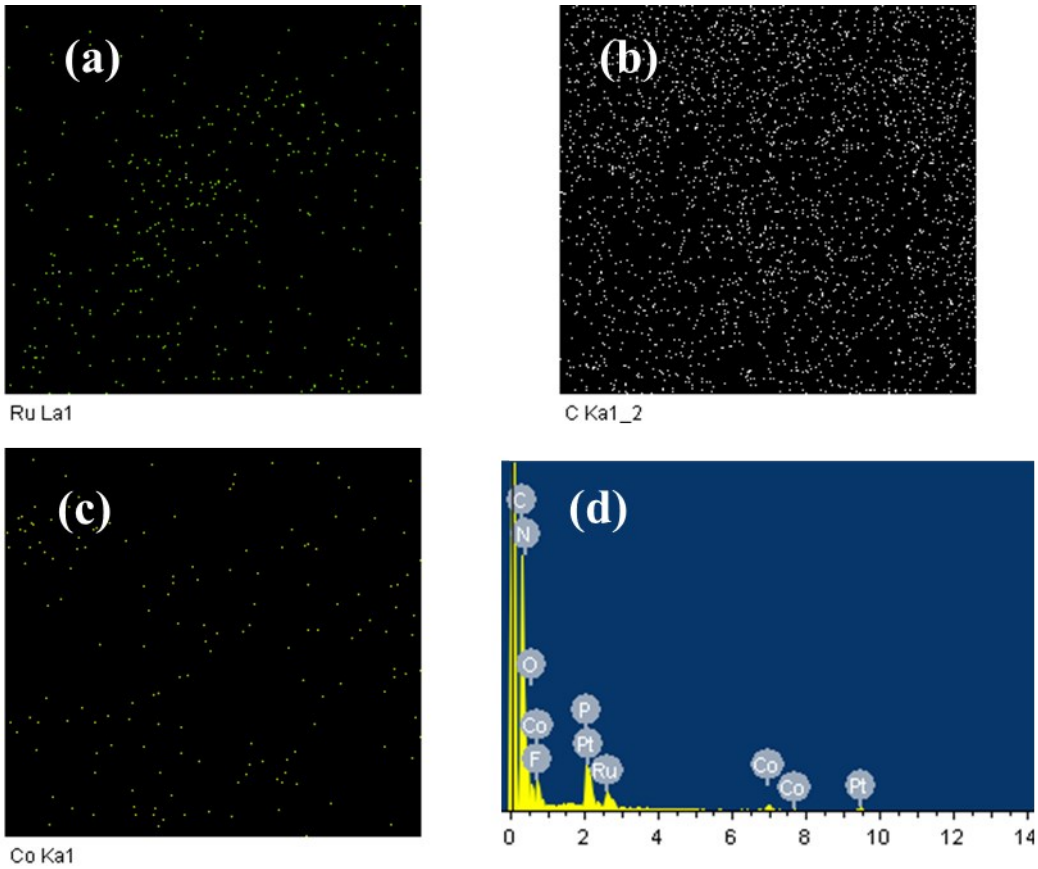

Fig. S6. (a-c) Elemental mapping and (d) EDS of RuL_2L'@200C_3N_4/MOF composite photocatalysts

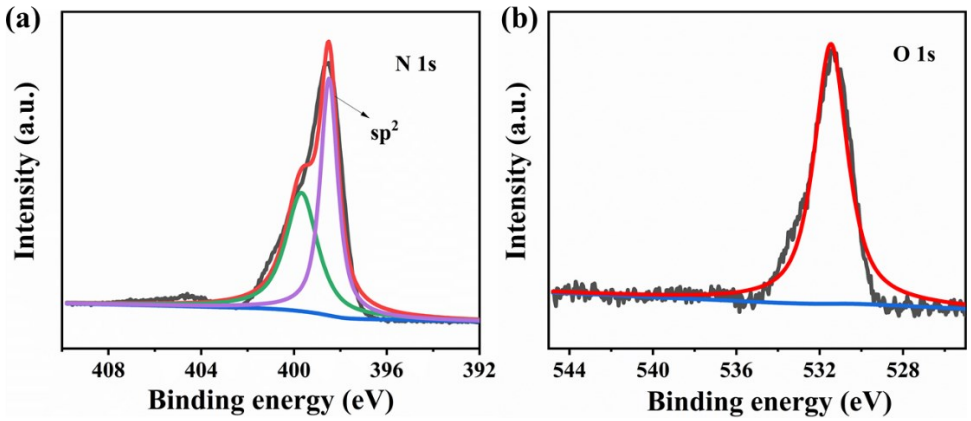

Fig. S7. XPS spectra of the RuL_2L'@200C_3N_4/MOF: N 1s (a) and O 1s (b)

Tab. S2. Specific surface areas, pore volumes and pore diameters for g-C_3N_4, RuL_2L'@C_3N_4/MOF and Co-MOF-74

Sample	$S_{BET}/m^2 \cdot g^{-1}$	$V_{pore}/cm^3 \cdot g^{-1}$	d_{pore}/nm
g-C_3N_4	4.8	0.025	18.3
RuL_2L'@C_3N_4/MOF	50.9	0.23	21.0
Co-MOF-74	530.0	0.28	25.8

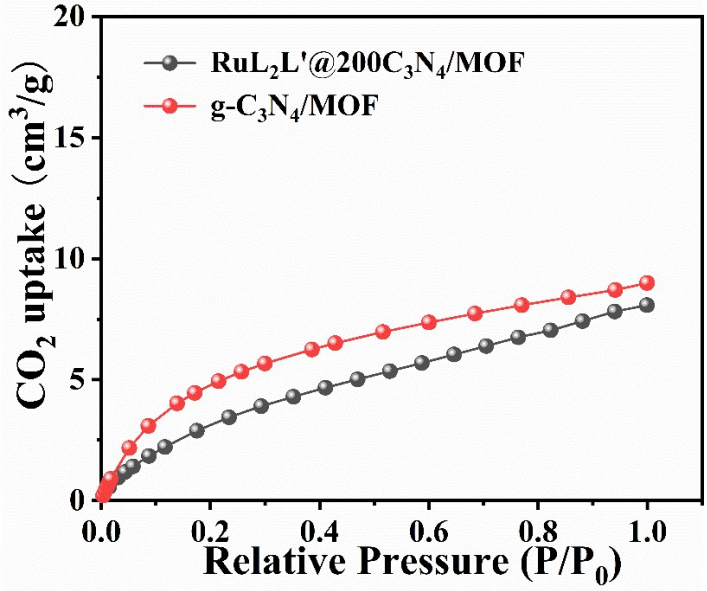

Fig. S8. CO_2 adsorption isotherms of the RuL_2L'@200C_3N_4/MOF and g-C_3N_4/MOF.

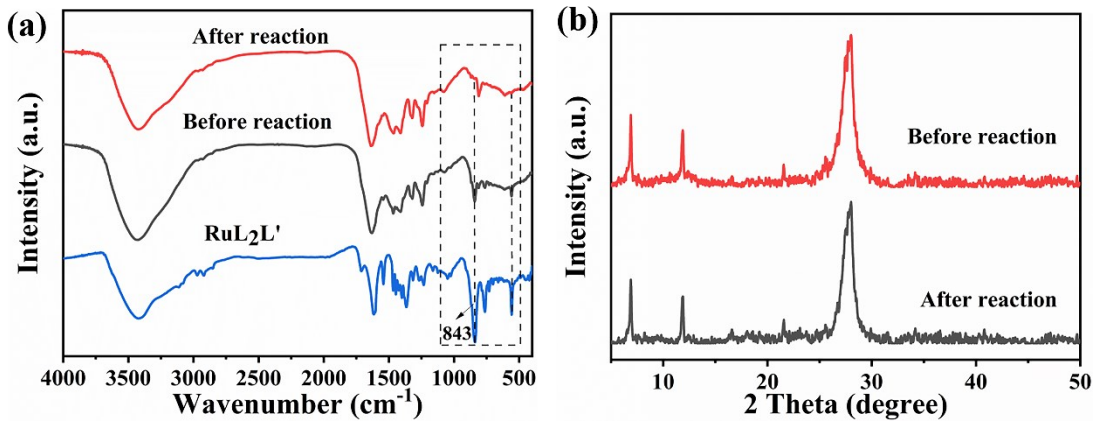

Fig. S9. FT-IR (a) and XRD (b) patterns of RuL_2L'@200C_3N_4/MOF before and after reaction

Tab. S3. ICP-MS of the $RuL_2L'@200C_3N_4$/MOF after every cycle

cycle times	content of RuL_2L'
1st	0.175
2th	0.098
3rd	0.054

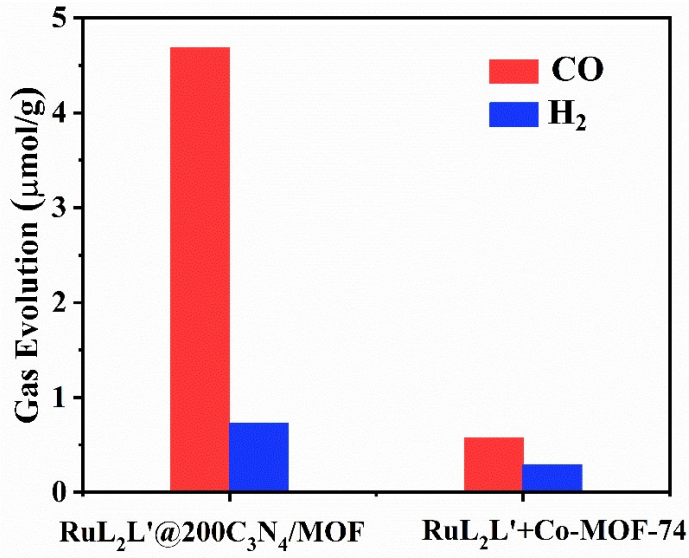

Fig. S10. The photocatalysis of $RuL_2L'@200C_3N_4$/MOF and RuL_2L' (0.168 mg) + Co-MOF-74 1 mg under the same reaction conditions.

Tab. S4. The production of samples within 3 hours under the same conditions

Condition	CO production (μmol/g)	H_2 production (μmol/g)
g-C_3N_4	3.9	trace
Co-MOF-74	10.8	trace
RuL_2L'	21.6	trace

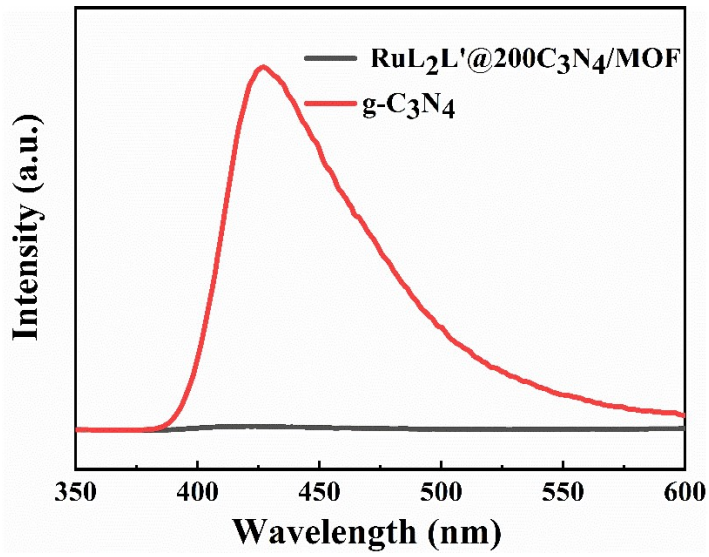

Fig. S11. PL spectra of g-C_3N_4 and RuL_2L'@C_3N_4/MOF

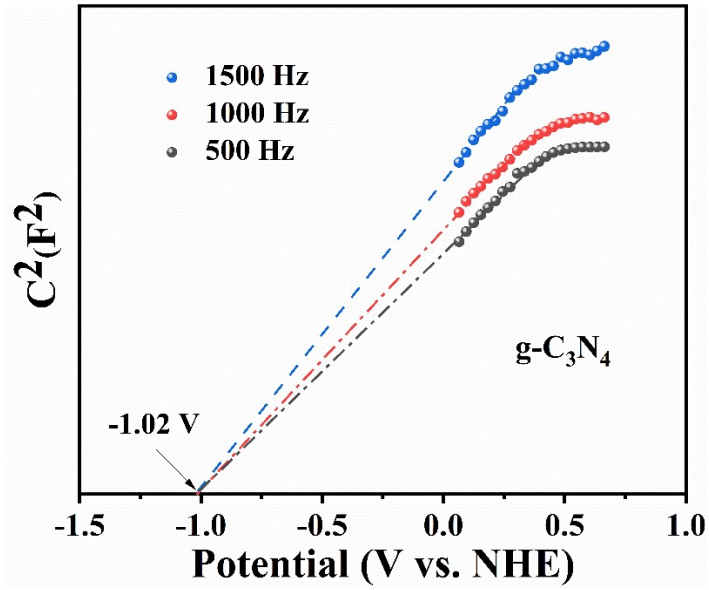

Fig. S12. The Mott-Schottky plots of g-C_3N_4.

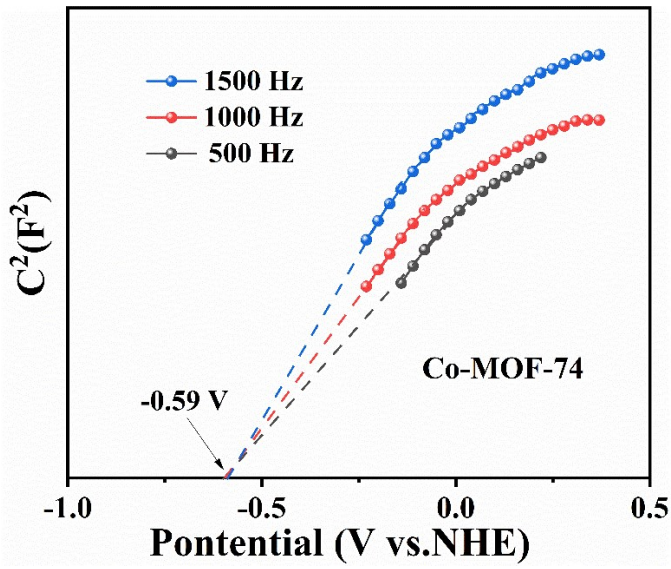

Fig. S13. The Mott-Schottky plots of Co-MOF-74.

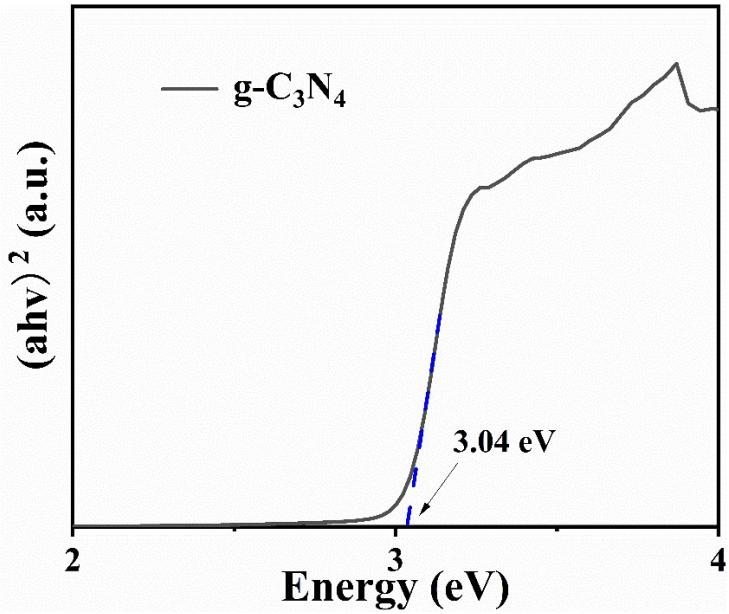

Fig. S14. The band gap spectra of g-C_3N_4.

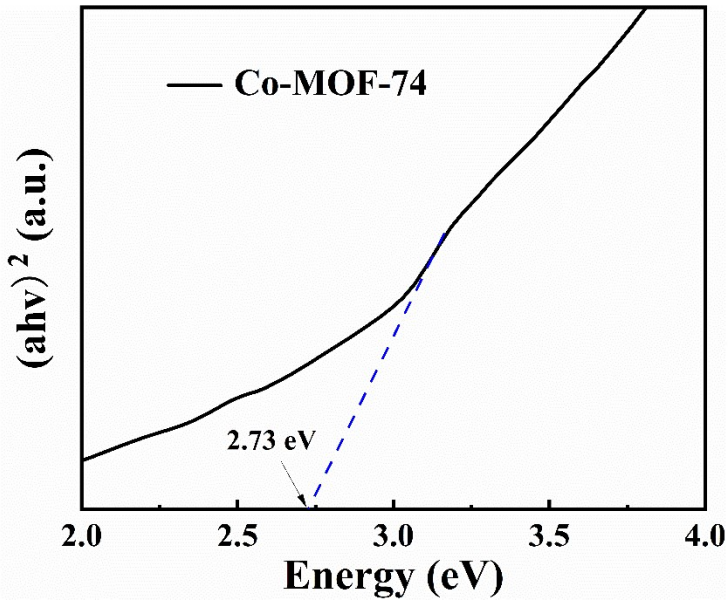

Fig. S15. The band gap spectra of Co-MOF-74.

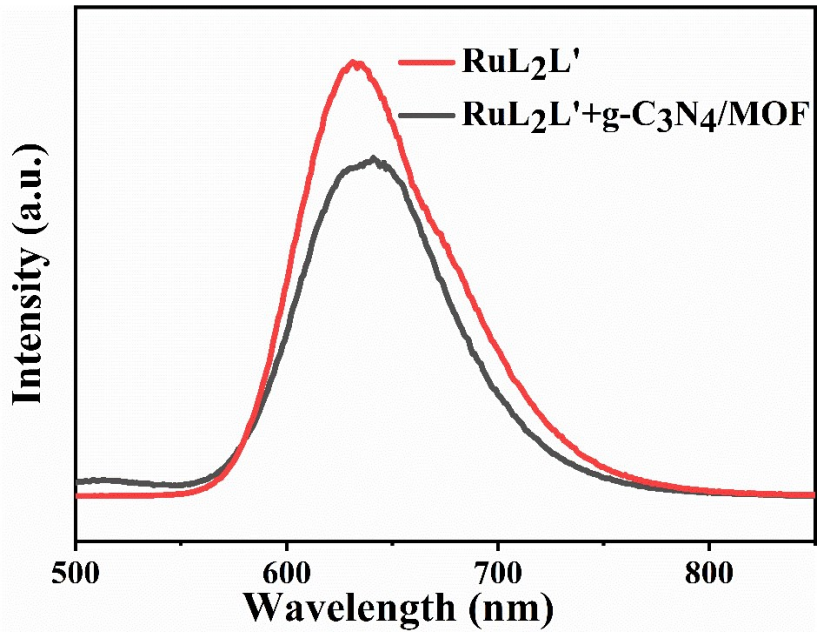

Fig. S16. PL spectrum of RuL_2L' in g-C_3N_4/MOF

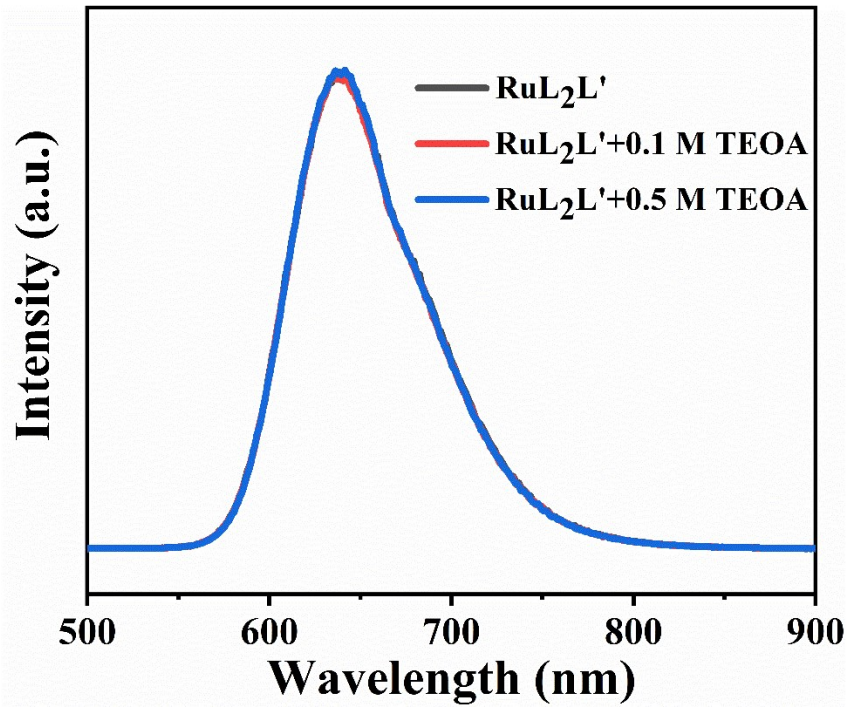

Fig. S17. PL spectrum of RuL_2L' with addition of TEOA (0, 100, 500 mM).

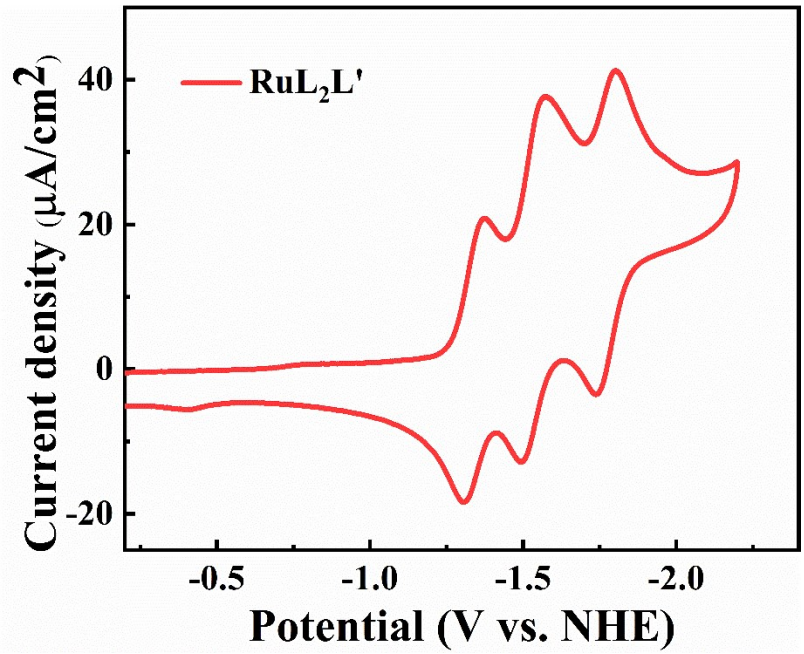

Fig. S18. The CV of RuL_2L' in CH_3CN with 0.1 M NBu_4PF_6 as supporting electrolyte under N_2 atmosphere.