Promoted CO_2 photoreduction toward HCOOH generation by nucleophilic effect in Co/Mg synergistic catalysis

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1.Materials and Characterizations

The ligand H_4TCPP was synthesized by a documented method. All the chemicals were of analytical grade and purchased from commercial sources without any further purification. ICP spectroscopy was conducted on Agilent 7500a Inductively Coupled Plasma Mass Spectrometry (ICP-MS 7500). TEM images were recorded on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. XPS was performed using an Escalab 250 instrument. Powder X-ray diffraction (PXRD) patterns were collected on a Siemens D5005 diffractometer with Cu-Kα radiation (λ=1.5418 Å) in the range of 5-40°at room temperature. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TG-7 analyzer heated from 30-800 °C at the heating rate of 10 °C·min^{-1} under a dry nitrogen gas atmosphere.

2.Computational calculation method

The ground-state geometry optimizations, vibrational frequency calculations were performed on the CoMg-TCPP and Co-TCPP catalyzed HCOOH formation at the B3LYP/[6-31G(d,p)/LanL2DZ(Co,Mg)] level. All calculations were carried out with the Gaussian 16 program [1].

3. Synthesis

Synthesis of Mg-TCPP

$Mg(NO_3)_2$•$6H_2O$ (60mg, 0.23 mmol) and H_4TCPP (10.0 mg, 0.017 mmol) were dissolved in the mixture of N, N'-dimethylacetamide (DMF 3 mL) and acetonitrile (1 mL) and nitric acid (60μL).The as-obtained mixture was transferred to a stainless steel Teflon-lined autoclave of 20 mL capacity. Stir at room temperature for 1 hour and place in a pre-heated oven at 130℃for 30h. Cool naturally to room temperature. The resulting colorless product was washed 3 times in DMF to remove other magazine ions from the solution [2].

Synthesis of Co-TCPP

Co $(NO_3)_2$·$6H_2O$ (35 mg, 0.12 mmol) and H_4TCPP (10.0 mg, 0.017 mmol) were dissolved in the

mixture of N, N'-dimethylacetamide (DMF 3 mL) and acetonitrile (1 mL) and nitric acid (50μL).The as-obtained mixture was transferred to a stainless steel Teflon-lined autoclave of 20 mL capacity. Stir at room temperature for 1 hour and place in a pre-heated oven at 130℃for 30h. Cool naturally to room temperature. The resulting mauve product was washed 3 times in DMF to remove other magazine ions from the solution [3].

4. Figures and Tables

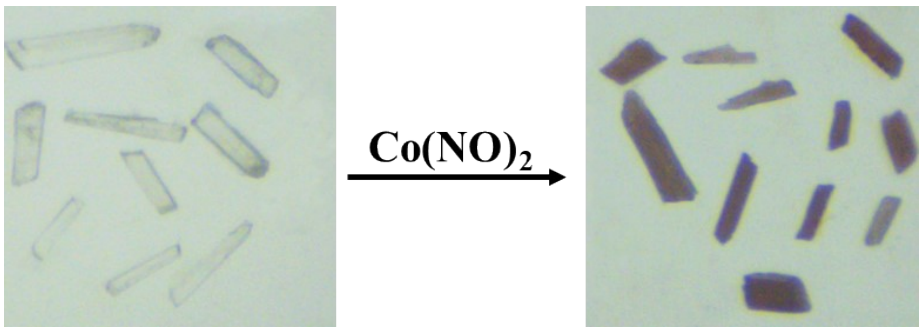

Fig. S1. Crystal before and after ion exchange.

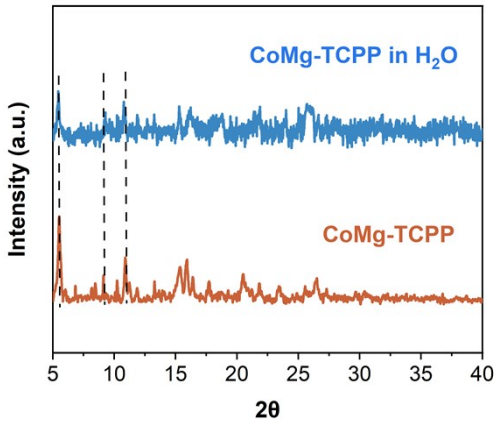

Fig. S2. PXRD of CoMg-TCPP after 48 h immersion in H_2O.

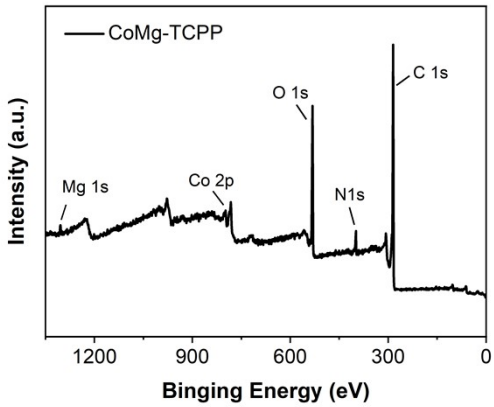

Fig. S3. The fully scanned spectrum of CoMg-TCPP.

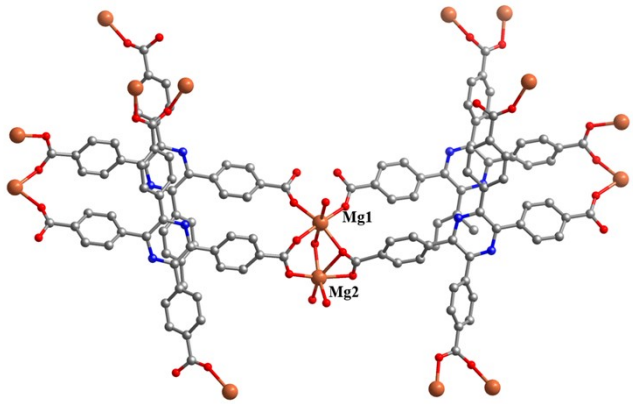

Fig. S4. The coordination-environment of Mg-TCPP.

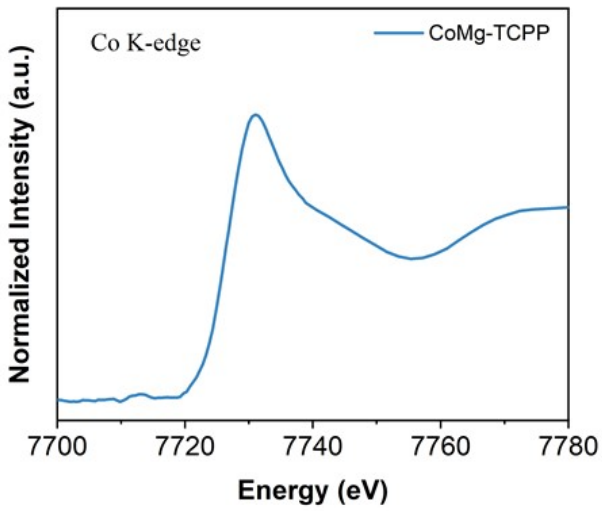

Fig. S5. Co K-edge XANES spectra of CoMg-TCPP.

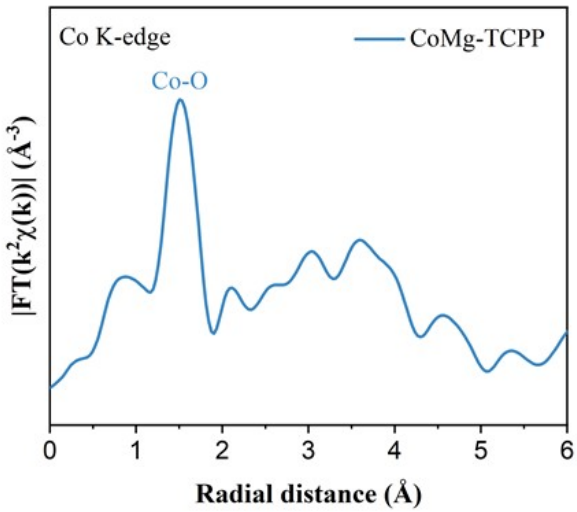

Fig. S6. Magnitude of k^2-weighed Fourier transforms of the Co K-edge EXAFS spectra of CoMg-TCPP.

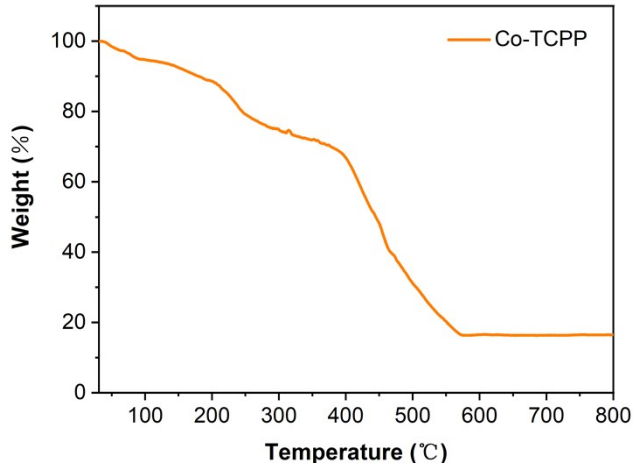

Fig. S7. TGA curves of Co-TCPP.

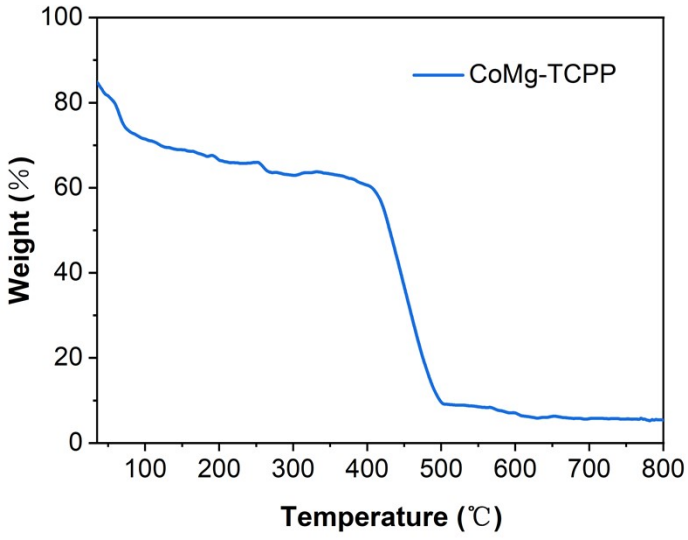

Fig. S8. TGA curves of CoMg-TCPP.

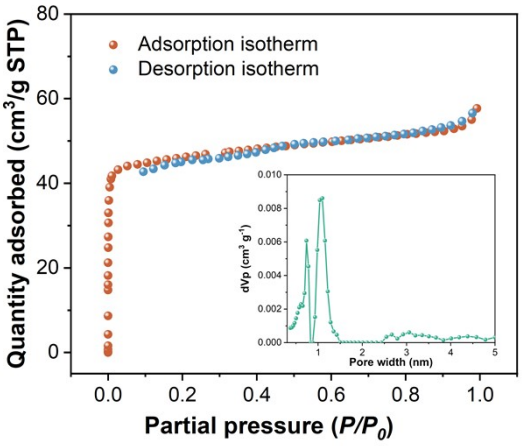

Fig. S9. N_2 adsorption and desorption isotherms of CoMg-TCPP at 77 K (inset: pore size distribution).

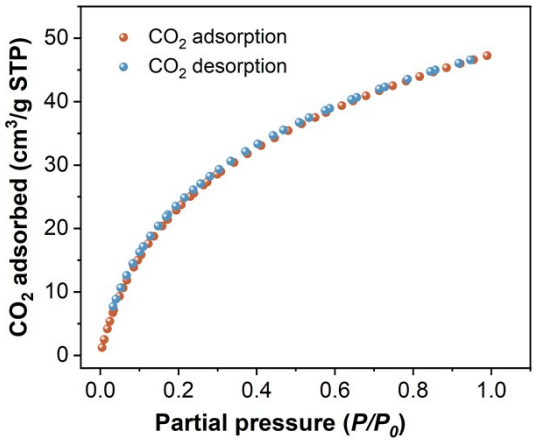

Fig. S10. CO_2 adsorption and desorption isotherms of CoMg-TCPP at 298 K.

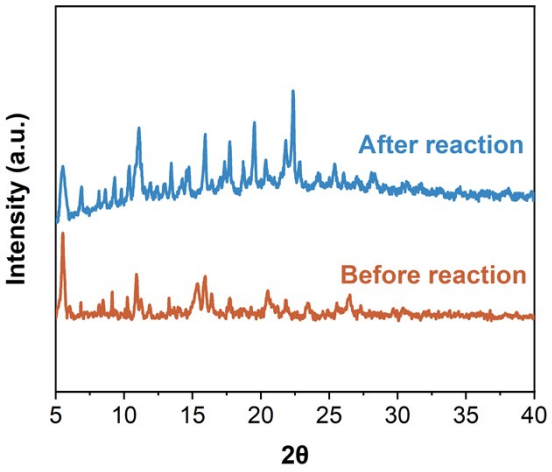

Fig. S11. PXRD of CoMg-TCPP before and after 2 h photocatalytic reaction.

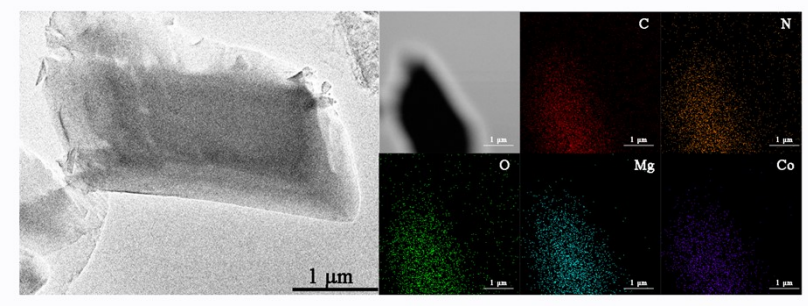

Fig. S12. HRTEM and EDS mapping images of CoMg-TCPP after photocatalytic reaction.

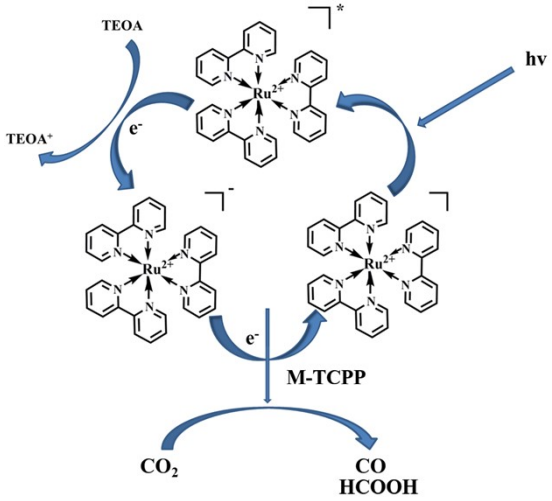

Fig. S13. Schematic of the CO_2 photocatalytic system

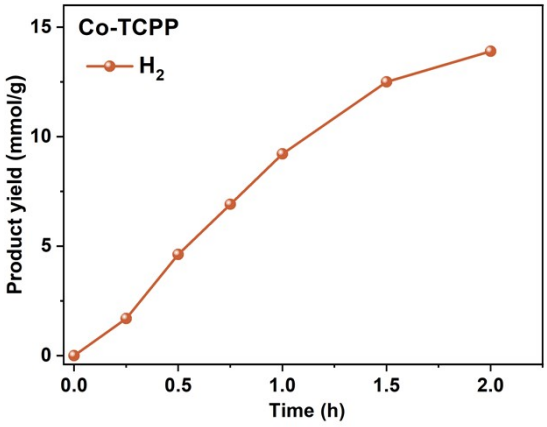

Fig. S14. Time-course profiles of H_2 catalyzed by Co-TCPP.

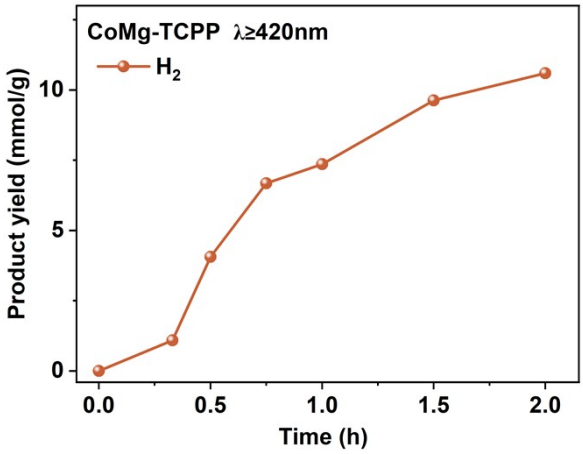

Fig. S15. Time-course profiles of H_2 catalyzed by CoMg-TCPP.

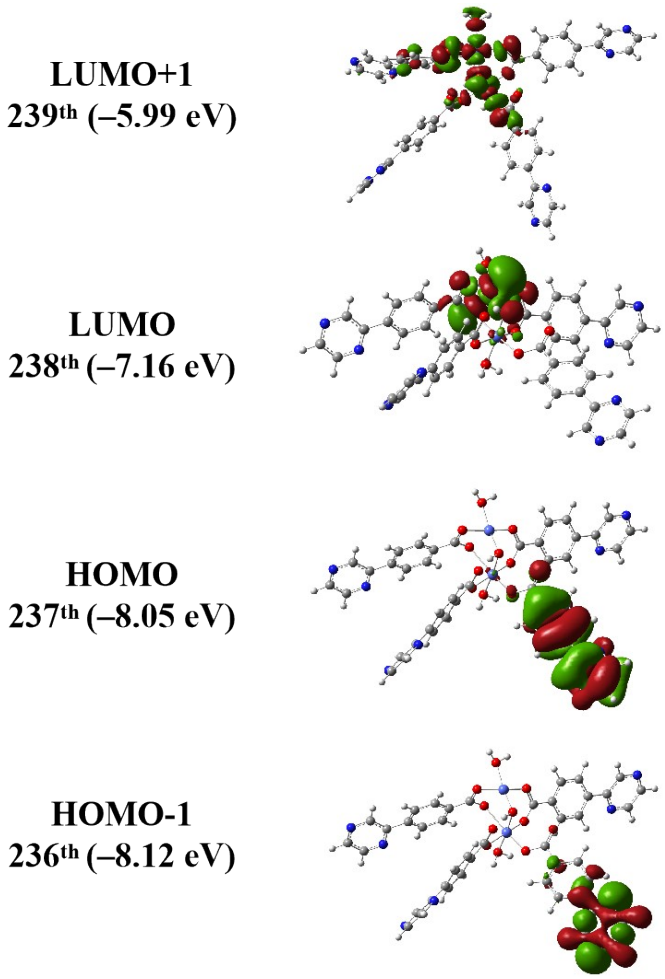

Fig. S16. The Kohn-Sham orbitals of Co-TPPP.

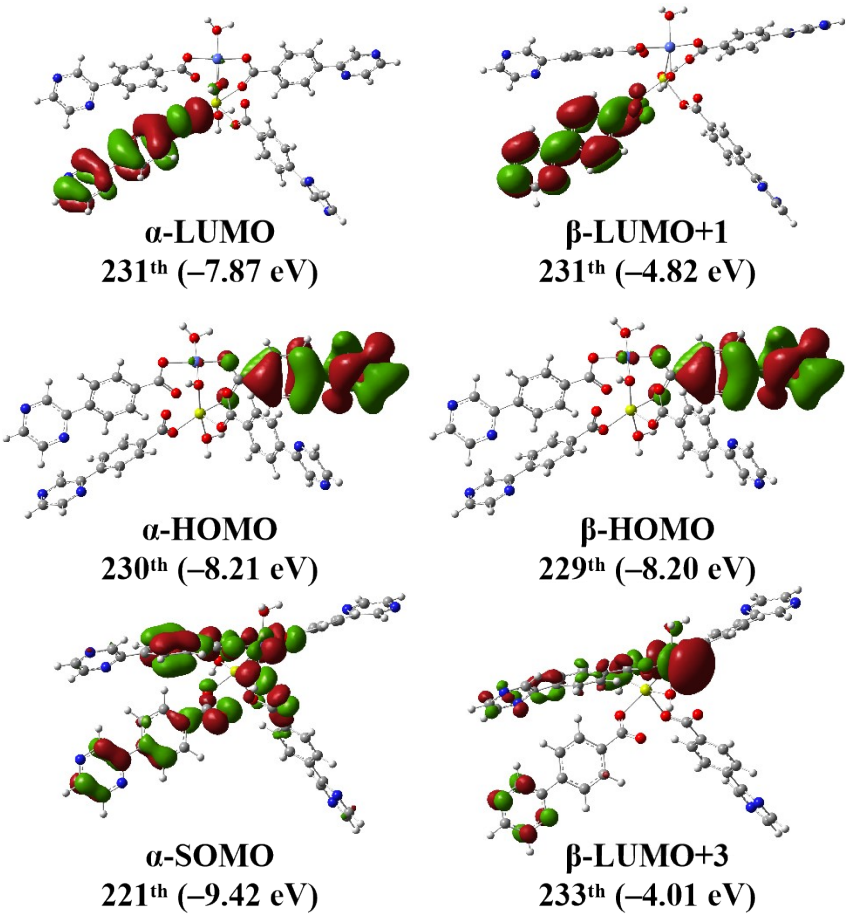

Fig. S17. The Kohn-Sham orbitals of CoMg-TPPP.

Table S1 Compared to other MOF-based photocatalytic CO_2 reduction of CO.

MOFs	Quantity	Light [nm]	Time [h]	CO [μmol]	H_2 [μmol]	Ref
Co-TCPP	1 mg	λ ⩾420	1	12.71	9.21	This work
CoMg-TCPP	1 mg	λ ⩾420	1	14.34	7.36	This work
MOF-Co	0.5 mg	λ ⩾420	5	22.8	25.3	
MOF-Ni	0.5 mg	λ ⩾420	12	22.3	0.52	[4]
MOF-Cu	0.5 mg	λ ⩾420	5	1.7	5.8	
Co-ZIF-9	0.8 μmol	λ ⩾420	0.5	41.8	29.9	
Co-MOF-74	0.8 μmol	λ ⩾420	0.5	11.7	14.6	[5]
Mn-MOF-74	0.8 μmol	λ ⩾420	0.5	1.5	1.8	
Co_6–MOF	0.005 mmol	λ ⩾420	0.5	3.73	2.81	[6]
Co-UiO-67	1 mg	400-800	4	13.2	49	[7]
Zr-DMBD	0.1 mg	λ =450	10	3.33	0.041	[8]

Table S2 Compared to other MOF-based photocatalytic CO_2 reduction of HCOOH.

MOFs	Time [h]	HCOOH [μmol]	Ref
CoMg-TCPP	1	940	This work
NH_2-UiO-66(Zr)	1	13.2	[9]
TFZS	3	1693	[10]
$Ni_{0.75}Mg_{0.25}$-MOF-74	1	638	[11]
Cu_2O-Pt/SiC/IrOx	1	896.7	[12]
UiO67-Ir-Cou 6/Cu	1	480.7	[13]
P@U	1	146	[14]
NH_2-C@Cu_2O	1	22.5	[15]
PCN-222	1	30	[16]
Co/NH_2-MIL-125(Ti)	1	38.4	[17]

Table S3 The research of reaction conditions of **Co-TCPP**.

Co-TCPP		
Entry	**CO [μmol]**	**H_2 [μmol]**
1[a]	12.71	9.21
2[b]	n.d.[c]	n.d.
3[d]	n.d.	n.d.
4[e]	0.25	0.51
5[f]	n.d.	0.77
6[g]	n.d.	n.d.

[a] Reaction conditions: $[Ru(bpy)_3]Cl_2·6H_2O$ (6 mg), Co-TCPP (1 mg) acetonitrile (MeCN, 4 mL), H_2O (1 mL), TEOA (1 mL), 30 °C, 1 h. [b] In the dark. [c] Not detectable. [d] Without $[Ru(bpy)_3]Cl_2·6H_2O$. [e] Without the Co-TCPP. [f] Using Ar to replace CO_2. [g] Without TEOA.

Table S4 The research of reaction conditions of **CoMg-TCPP**.

CoMg-TCPP		
Entry	**CO [μmol]**	**H_2 [μmol]**
1[a]	14.34	7.36
2[b]	n.d.[c]	n.d.
3[d]	n.d.	n.d.
4[e]	0.25	0.51
5[f]	n.d.	0.63
6[g]	n.d.	n.d.
7[h]	7.46	23.57

[a] Reaction conditions: $[Ru(bpy)_3]Cl_2·6H_2O$ (6 mg), CoMg-TCPP (1 mg) acetonitrile (MeCN, 4 mL), H_2O (1 mL), TEOA (1 mL), 30 °C, 1 h. [b] In the dark. [c] Not detectable. [d] Without $[Ru(bpy)_3]Cl_2·6H_2O$. [e] Without the CoMg-TCPP. [f] Using Ar to replace CO_2. [g] Without TEOA. [h]Using CH_3OH to replace MeCN.

Table S5 The research of reaction conditions of **CoMg-TCPP**.

Entry	HCOOH [μmol/g]
1	940
2[b]	n.d.[c]
3[d]	n.d.
4[e]	n.d.
6[f]	n.d.
8[g]	n.d.

[a] Reaction conditions: $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (6 mg), CoMg-TCPP (1 mg) acetonitrile (MeCN, 4 mL), H_2O (1 mL), TEOA (1 mL), 30 °C, 1 h. [b] In the dark. [c] Not detectable. [d] Without $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$. [e] Without the CoMg-TCPP. [f] Using Ar to replace CO_2. [g] Without TEOA.

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