

Supporting information for

## Photocatalytic CO<sub>2</sub> Reduction to CO Catalysed by Lanthanide Complexes

Yingzhe Zhao,<sup>a,b</sup> Jianling Zhang,<sup>\*a,b</sup> Haoxiang Wang,<sup>a,b</sup> Renjie Zhang,<sup>a,b</sup> Yunan Teng,<sup>a,b</sup> Meiling Li,<sup>a,b</sup> Yi Song<sup>a,b</sup> and Zhonghao Tan<sup>a,b</sup>

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (P. R. China).

<sup>b</sup> School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049 (P. R. China)

\* Corresponding author e-mail: zhangjl@iccas.ac.cn

## Experimental Section

### 1. Materials

Chemicals used, providers and purities are listed below. Cerium(III) chloride heptahydrate, Aladdin, 99%. Lanthanum(III) chloride heptahydrate, Macklin, 99.9%. Praseodymium(III) heptahydrate, Macklin, 99%. Neodymium(III) chloride hexahydrate, Energy Chemical, 99.99%. Samarium(III) chloride hexahydrate, Macklin, 99%. Europium(III) chloride hexahydrate, Macklin, 99.99%. Gadolinium(III) chloride hexahydrate, Macklin, 99%. Terbium(III) chloride hexahydrate, Macklin, 99.9%. Dysprosium(III) chloride hexahydrate, Macklin, 99.9%. Holmium(III) chloride hexahydrate, Macklin, 99.9%. Erbium(III) chloride hexahydrate, Macklin, 99.5%. Thulium(III) chloride hexahydrate, Macklin, 99.5%. Ytterbium(III) chloride hexahydrate, Macklin, 99.9%. Lutetium(III) chloride hexahydrate, Macklin, 99.99%. 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd), Energy Chemical, 99%. Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ( $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ), Innochem, 99%. Sodium hydroxide (NaOH), Sinopharm, A. R. Tetrabutylammonium bromide ( $\text{TBAPF}_6$ ), Macklin, 98%. Mesitylene, Innochem, 98%. Dimethyl sulfoxide deuterated ( $\text{DMSO-d}_6$ ), Innochem, 99.8%. 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), Dojindo,  $\geq 99\%$ . Acetonitrile, Concord, G.R. Ethyl acetate, Concord, G. R. Distilled water, Beijing Analytical Instrument Factory, A. R. All reagents were used directly without any further purification.

### 2. Synthesis of catalysts

144 mg of NaOH was dissolved in 10 mL water, then 626  $\mu\text{L}$  of Htmhd was added dropwise under vigorously stirring. 1 mmol of lanthanide chloride was dissolved in 5 mL water, followed by adding dropwise into the mixture above. The mixture was left stirring for another half an hour, then the precipitate was collected by centrifugation, washed with water twice, and dried under vacuum at 60 °C overnight. The dried solid was extracted by ethyl acetate and centrifuged. The supernatant was evaporated on a rotavapor to exclude the solvent. The crystal obtained was collected and used in the subsequent catalysis experiments.

### 3. Characterizations

Single crystal X-ray diffraction was carried out on a Rigaku MM007HF diffractometer from Japan. HRMS spectra were measured on a Bruker Solarix mass spectrometer from Germany. Infrared spectra were obtained via a Bruker Vertex 70v Fourier transform infrared spectrometer from Germany via potassium bromide tablets as carrier. UV-vis spectra of the photocatalysts were measured on a Shimadzu UV-2600i UV-vis spectrometer from Japan, with samples dissolved in acetonitrile at a concentration of 0.1 g  $\text{L}^{-1}$ . Cyclic voltammetry curves were scanned on a CHI660E electrochemistry workstation from China, with glassy carbon as working electrode, platinum wire as auxiliary electrode and saturated calomel electrode as reference electrode. The photocatalyst was dissolved in acetonitrile at a concentration of 1.0 g  $\text{L}^{-1}$ , with 0.10 mol  $\text{L}^{-1}$   $\text{TBAPF}_6$  as supporting electrolyte.

### 4. Photocatalytic tests

Photocatalytic performances of the catalysts were tested in a quartz reactor under a 300 W Xe Lamp (CEAulight CEL-HX, China). 7 mg photocatalyst and 2 mg  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  were dissolved in

10 mL H<sub>2</sub>O/acetonitrile solution with a certain amount of water. CO<sub>2</sub> was bubbled into the system for 30 min to saturate the solution and drive out the residue air in the reactor. Then the photocatalytic process was carried out under Xe lamp irradiation. The temperature of the reactor was controlled by circulating water at 25±5 °C. Then a sample of the gas in the reactor was examined by gas chromatography (Agilent GC-8890B, USA) to determine the amount of gaseous product. The liquid products were detected by <sup>1</sup>H nuclear magnetic resonance (Bruker Avance III 400 HD, Switzerland) using DMSO-d<sub>6</sub> as deuterated solvent and mesitylene as inner standard.

### **5. Fluorescence quenching of photosensitizer**

Quenching of the fluorescence of photosensitizer by series of photocatalysts was observed via a Horiba FluoroMax+ fluorescence spectrometer from France. The excitation wavelength was fixed at 482 nm. Emission spectra of acetonitrile solution of 200 mg L<sup>-1</sup> Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and certain concentrations of lanthanide complex were scanned. The concentration of Ce(tmhd)<sub>4</sub> was set at 0, 140, 280, 420, 560 and 700 mg L<sup>-1</sup>, respectively. The concentrations of other complexes were set at 700 mg L<sup>-1</sup>.

### **6. Electron paramagnetic resonance (EPR) test**

7 mg Ce(tmhd)<sub>4</sub>, 2 mg Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O was dissolved in a 10 mL H<sub>2</sub>O/acetonitrile solution (10 vol% water contained). 0.6 mL solution above was taken out, bubbled CO<sub>2</sub> until saturated, and was added 12 μL DMPO. The mixture was irradiated under 300 W Xe lamp (CEAulight CEL-HX, China) for 1 min. The solution before and after light irradiation was analysed using Bruker ELEXSYS II E500 from Germany to get EPR spectra.

## Results

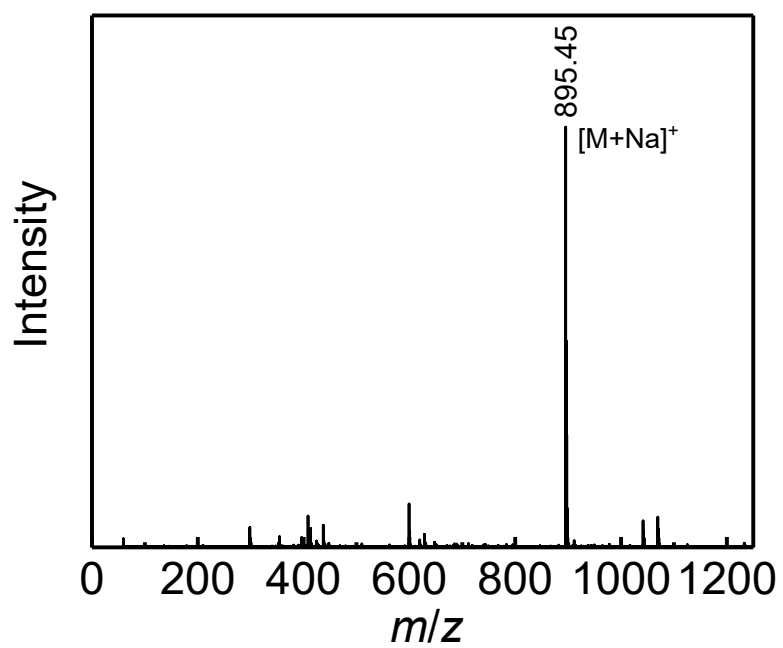
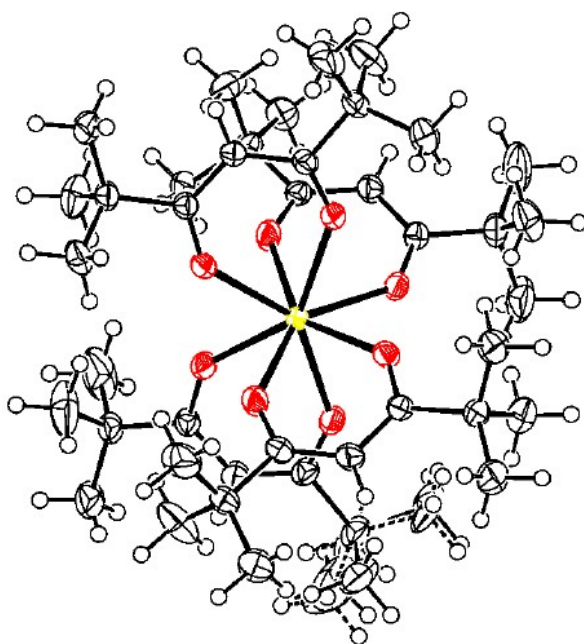
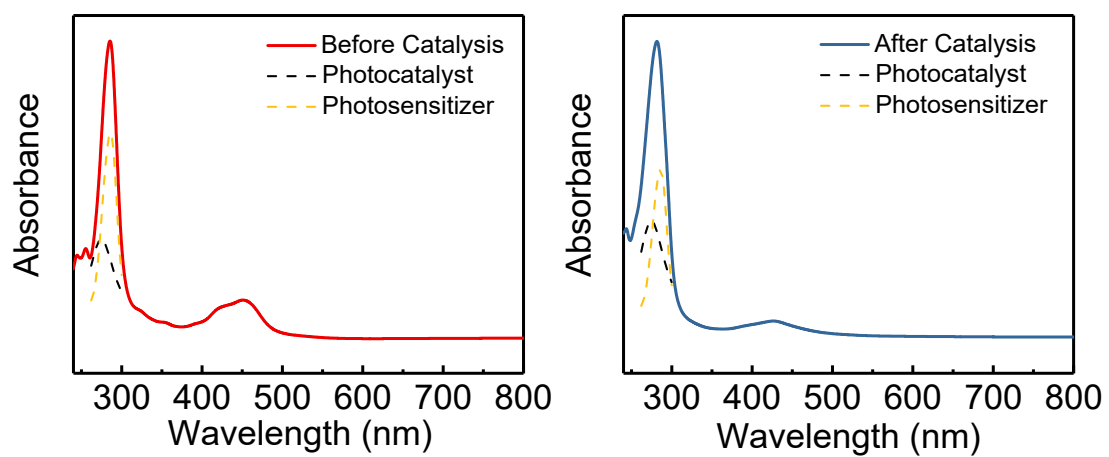


Fig. S1 HRMS spectrum of  $\text{Ce}(\text{tmhd})_4$



**Fig. S2 Ellipsoid diagram of Ce(tmhd)<sub>4</sub>. Yellow: cerium; red: oxygen; black ellipsoid: carbon; hollow black sphere: hydrogen.**



**Fig. S3 UV-vis spectrum of reaction system before (left) and after catalysis (right) and peak fitting.**

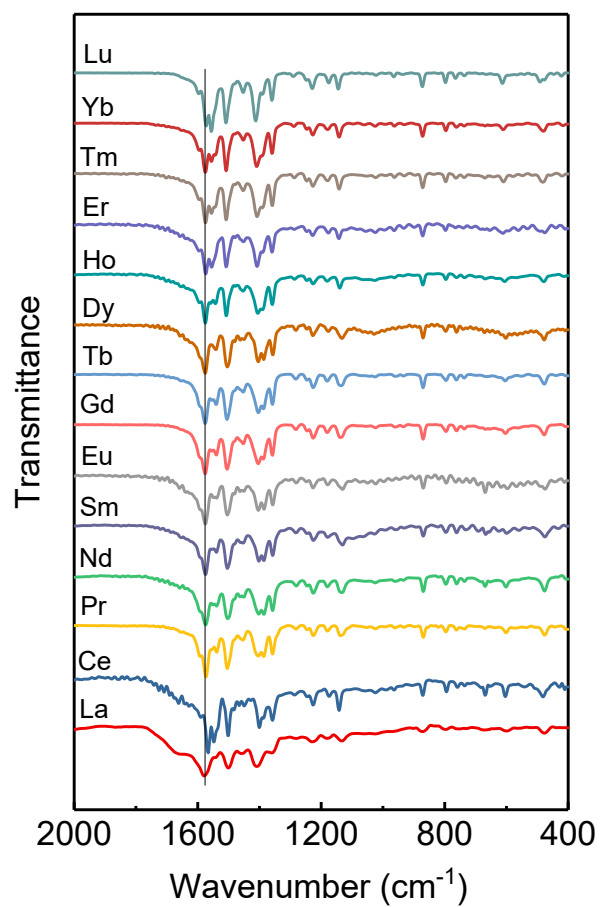


Fig. S4 Infrared spectra of lanthanide complexes with ligand of Htmhd.

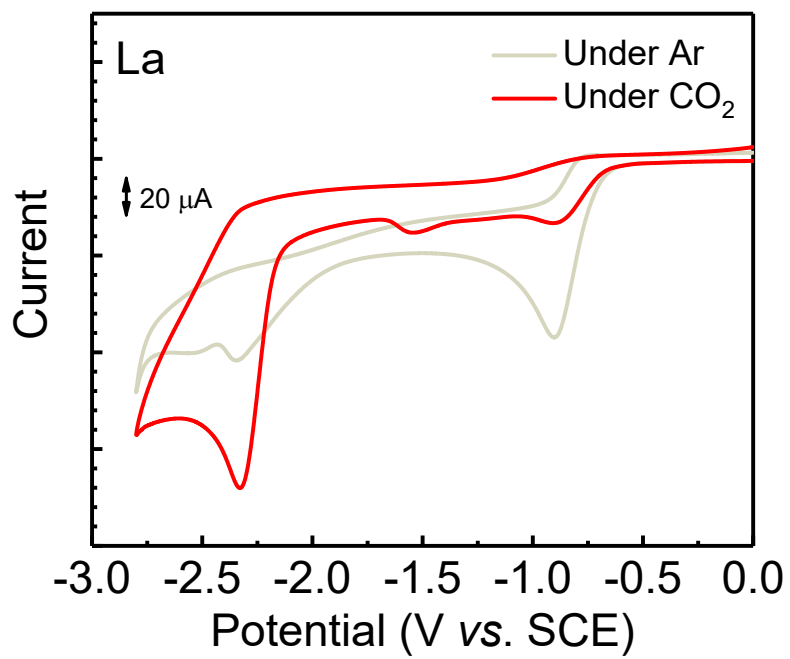


Fig. S5 Cyclic voltammety curve of  $\text{La(tmhd)}_3$ .



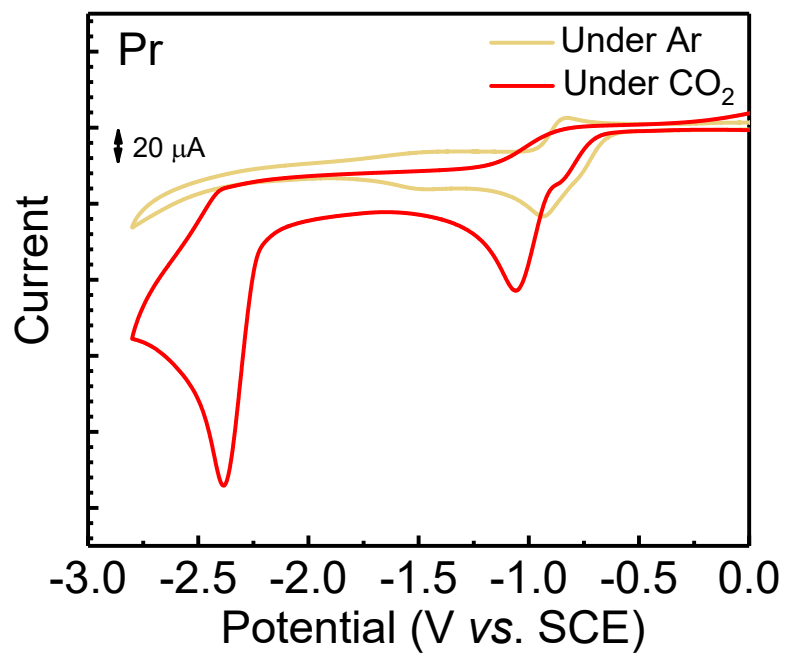


Fig. S6 Cyclic voltammetry curve of Pr(tmhd)<sub>3</sub>.

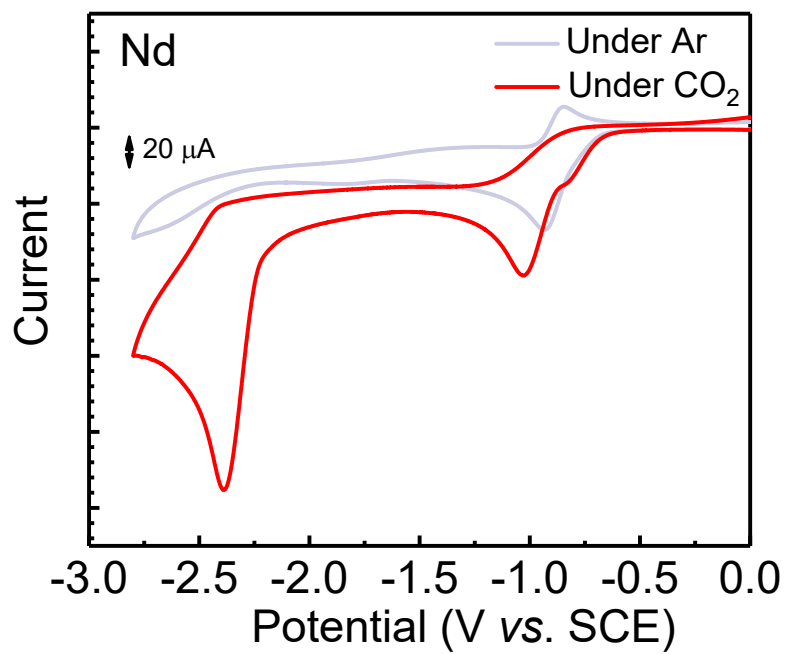


Fig. S7 Cyclic voltammetry curve of Nd(tmh)<sub>3</sub>.

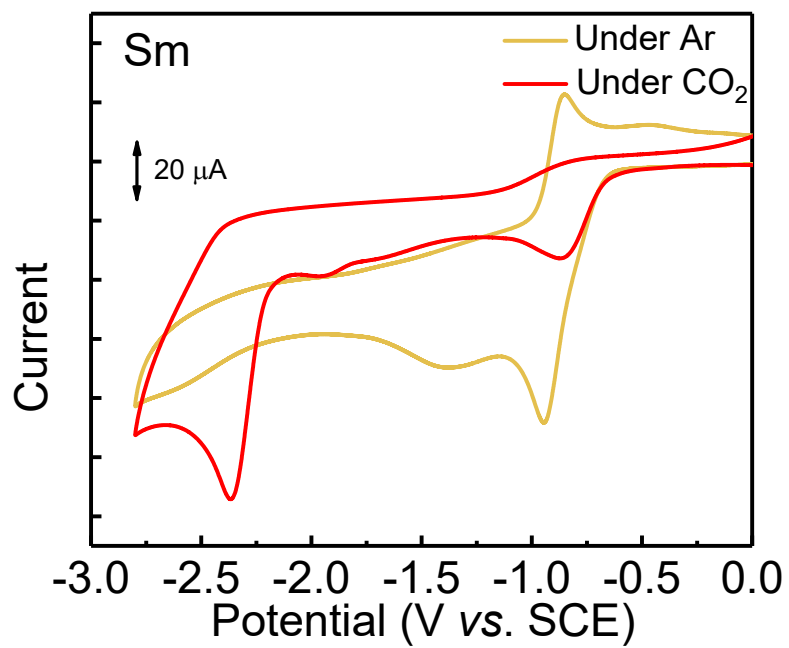


Fig. S8 Cyclic voltammetry curve of Sm(tmd)<sub>3</sub>.

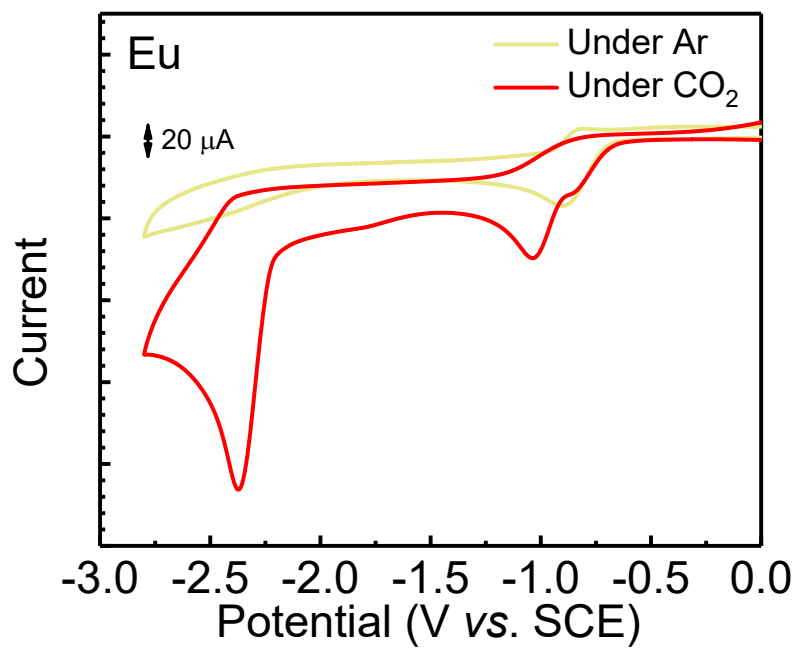


Fig. S9 Cyclic voltammetry curve of  $\text{Eu}(\text{tmhd})_3$ .

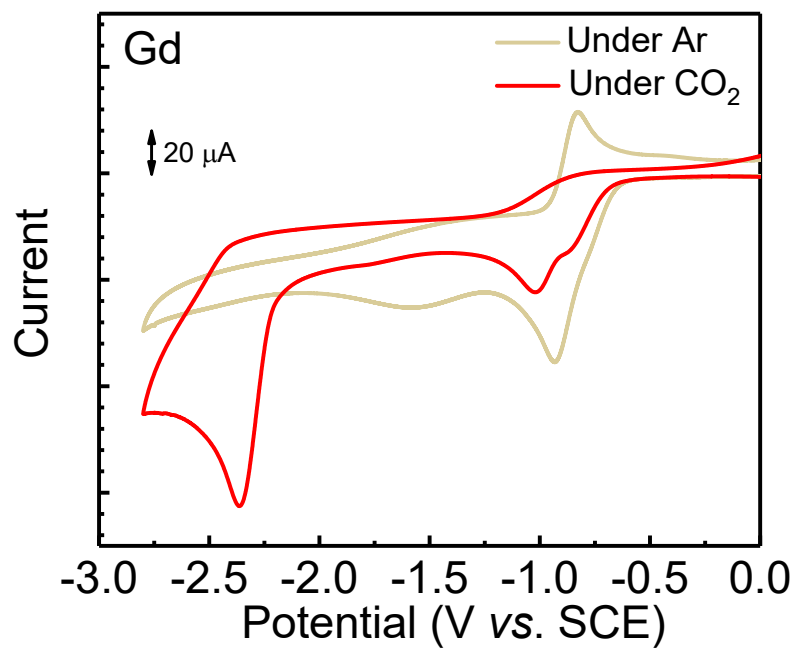


Fig. S10 Cyclic voltammetry curve of Gd(tmhd)<sub>3</sub>.

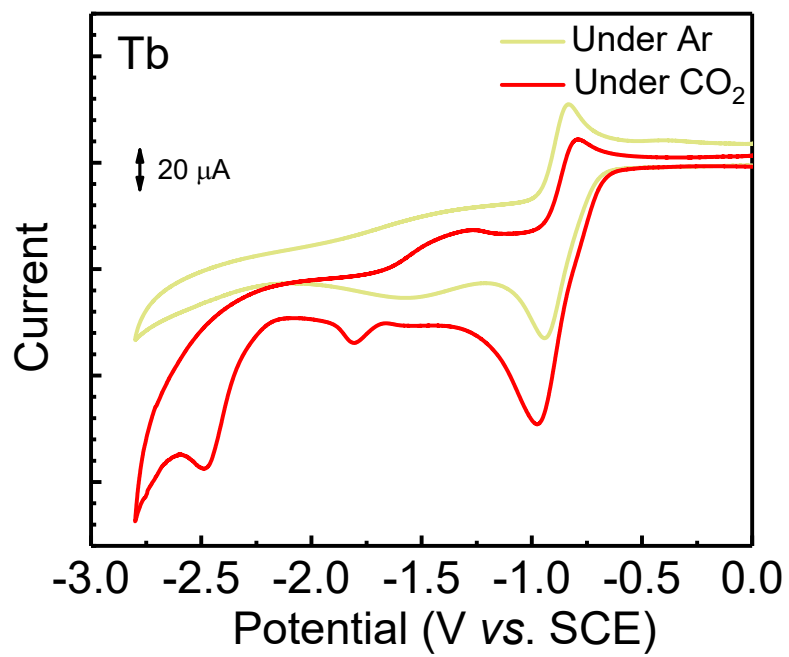


Fig. S11 Cyclic voltammetry curve of Tb(tmhd)<sub>3</sub>.

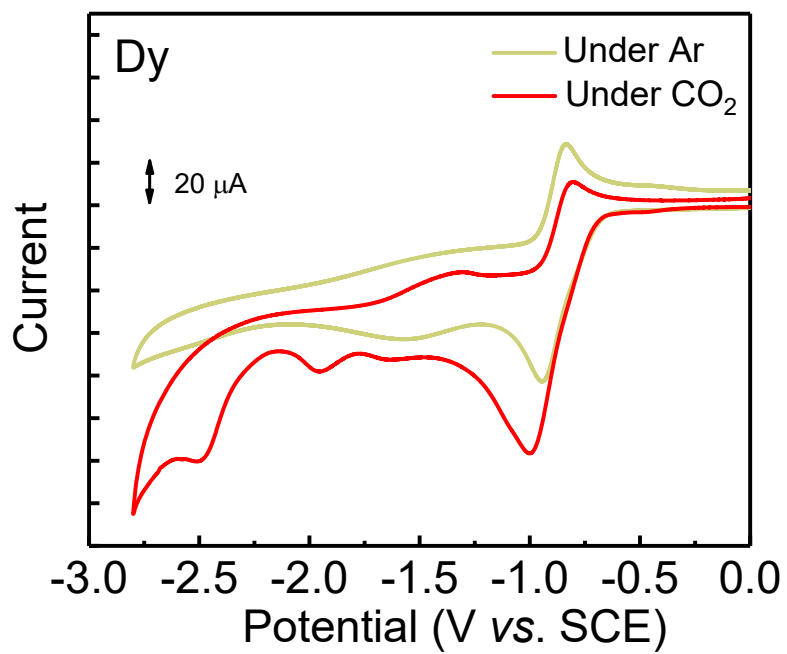


Fig. S12 Cyclic voltammetry curve of Dy(tmhhd)<sub>3</sub>.

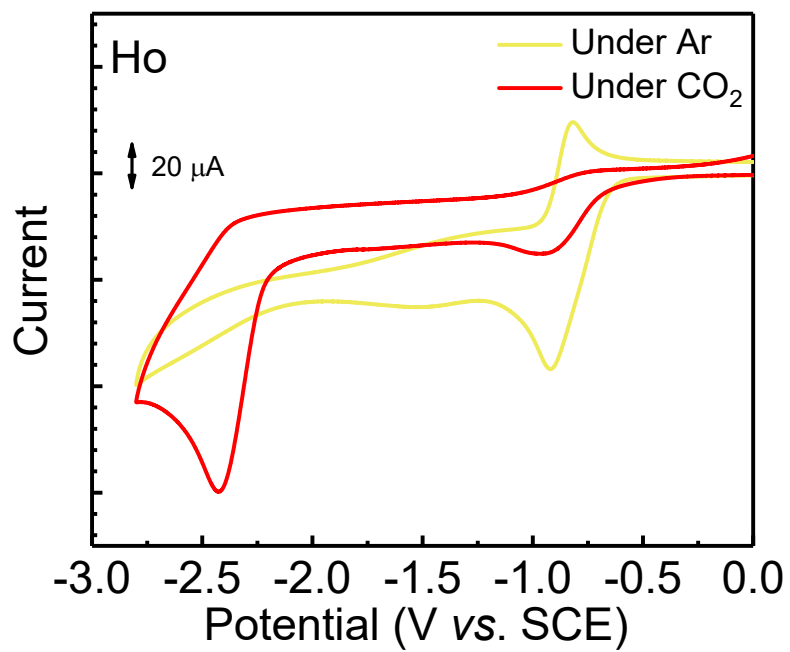


Fig. S13 Cyclic voltammetry curve of Ho(tmhd)<sub>3</sub>.



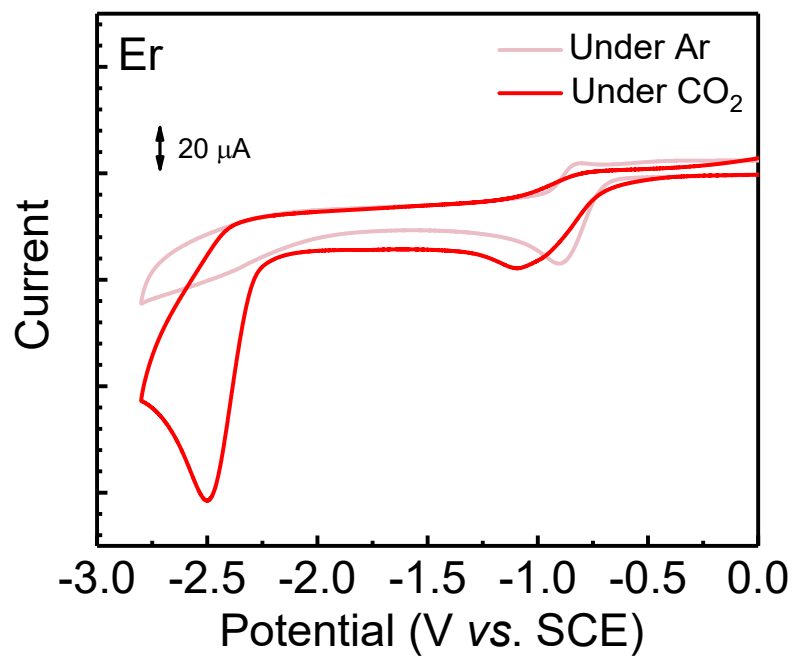


Fig. S14 Cyclic voltammetry curve of  $\text{Er(tmhd)}_3$ .

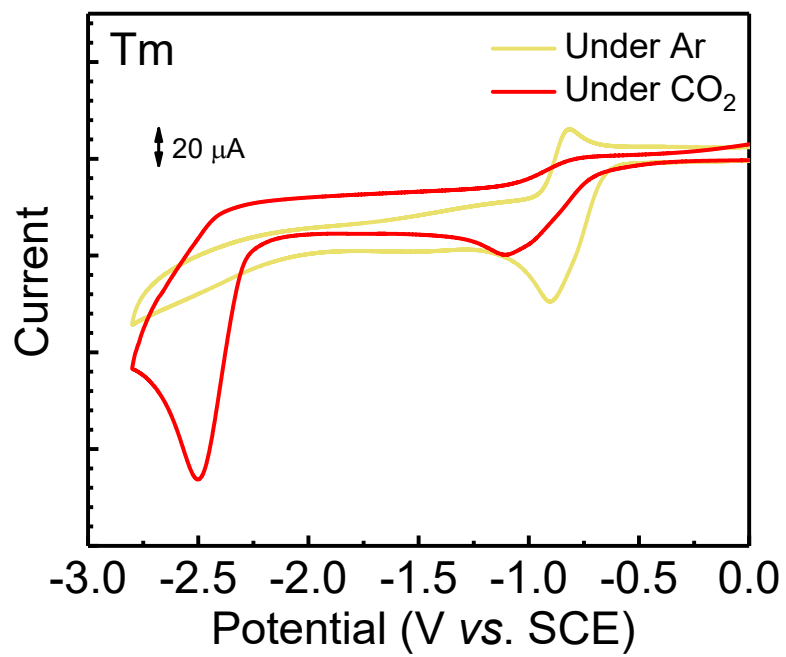


Fig. S15 Cyclic voltammetry curve of  $Tm(tmhd)_3$ .

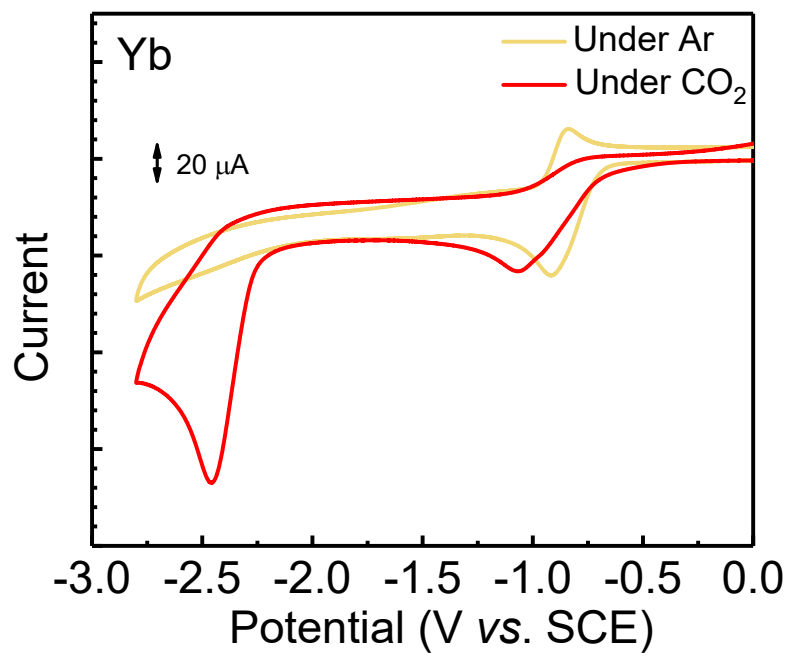


Fig. S16 Cyclic voltammetry curve of  $\text{Yb}(\text{tmhd})_3$ .

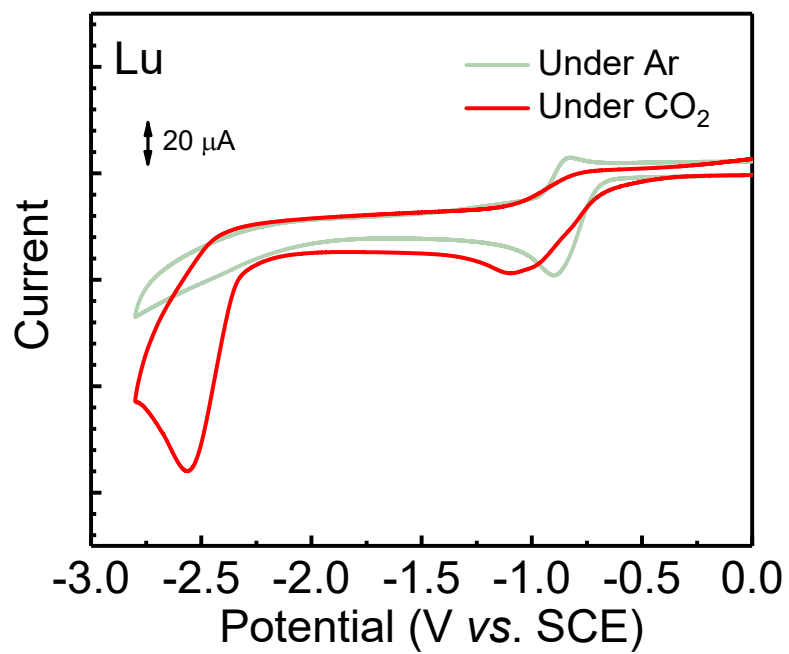


Fig. S17 Cyclic voltammetry curve of Lu(tmhd)<sub>3</sub>.

**Table S1 Crystallographic data of Ce(tmhd)<sub>4</sub>**

Formula	C <sub>44</sub> H <sub>76</sub> CeO <sub>8</sub>
Crystal system	Triclinic
<i>a</i> /Å	12.3244(2)
<i>b</i> /Å	19.5919(3)
<i>c</i> /Å	21.1768(3)
<i>V</i> /Å <sup>3</sup>	4827.44(13)
<i>α</i> /°	82.7350(10)
<i>β</i> /°	89.9610(10)
<i>γ</i> /°	72.2690(10)
<i>R</i> <sub>1</sub>	0.0245
<i>wR</i> <sub>2</sub>	0.0634
GooF	1.031
Temp./K	170

**Table S2 Comparison of photocatalytic CO<sub>2</sub> reduction to CO**

Catalysts	Reaction System	Irradiation light	CO evolution rate ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Selectivity (%)	Ref.
Co(OH) <sub>2</sub> /CdS	Gas-solid	Xe lamp, >420 nm	8.11	~100	1
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub>	1 M NaHCO <sub>3</sub> aqueous solution	254±10 nm	0.04	14	2
Sr-doped NaTaO <sub>3</sub>	0.1 M NaHCO <sub>3</sub> aqueous solution, Ag as cocatalyst	High pressure Hg lamp	352	86	3
Ag/BaTi <sub>4</sub> O <sub>9</sub>	pH=9 NaHCO <sub>3</sub> aqueous solution	254±10 nm	19	>99	4
Ag-Bi <sub>2</sub> WO <sub>6</sub>	Gas-solid	Xe lamp	116.96	95.7	5
Bi <sub>2</sub> MoO <sub>6-x</sub> /MoS <sub>2</sub>	Water	Xe lamp	29.01	92.45	6
Ag <sub>0.19</sub> /TJU-16	Water	Xe lamp	10.1	50.25	7
MAPbI <sub>3</sub> @PCN-221(Fe <sub>0.2</sub> )	Ethyl acetate/water solution	Xe lamp	8.7 (CH <sub>4</sub> 27.1)	7.4 (CH <sub>4</sub> 92.6)	8
CNGA/CdS	Water	Xe lamp, >420 nm	32.75	~100	9
CaW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub>	Water	254 nm	22.3	37	10
COF:g-C <sub>3</sub> N <sub>4</sub> heterojunction	Water, pressure at 1.75 bar	UV	7.56	100	11
Ce(tmhd) <sub>4</sub>	Water/acetonitrile solution	Xe lamp	78	>99	This work

## References

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