Electronic Supplementary Information (ESI)

Silver-frameworks based on tetraphenylethylene-imidazole ligand for electrocatalytic reduction of CO_2 to CO

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Materials and characterizations

The reagents used in the experiment were purchased and used directly without any post-treatment and purification. Silver nitrate ($AgNO_3$), 4,4'-oxybisbenzoic acid (H_2OBA), silver trifluoromethanesulfonate ($AgCF_3SO_3$) and potassium hydroxide (KOH) were purchased from Shanghai Titan Science Co., Ltd. Nafion reagent (5 wt%) was purchased from Sign Aldrich. Acetonitrile and isopropanol were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. 1,1,2,2-Tetrakis(4-(imidazol-1-yl)phenyl)ethene (TIPE) was synthesized according to the literature procedure.[1] Water used in the material preparation process is deionized water (18.25 Ω).

Powder X-ray diffraction patterns (PXRD) of the samples were measured on the Bruker D8 Advance X-ray diffractometer using Cu-Kα (λ = 1.5418 Å) radiation. During the testing process, the voltage of the instrument was 40 kV, the current was 40 mA. The total reflection infrared (ATR-IR) spectra of the samples were measured on the Fourier transform infrared (FT-

IR) spectrometer TENSOR 27 with a spectral range of 4000-400 cm^{-1}. TG data of the samples were obtained through testing on a Mettler-Toledo (TGA/DSC1) thermal analyzer, and thermogravimetric analysis was performed under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Elemental content of the samples was determined by Elementar UNICUBE element analyzer. Transmission electron microscopy (TEM) images were obtained on JEOL-2010. Cyclic voltammetry (CV) profiles and electrochemical impedance spectroscopy (EIS) were performed on the Zahner electrochemical workstation (IM6ex, Zahner Scientific Instruments, German).

X-ray crystallography

Crystallographic data of the samples were collected on the Bruker D8 Venture and the Bruker smart apex II CCD area detector diffractometer. φ/ω scanning was performed with graphite monochromators Ga-Kα (λ = 1.34133a) and Mo-Kα (λ = 0.71073 A), and the crystals were maintained at 193 K during data collection. The structures were solved by direct methods with SHELXT-2014, expanded by subsequent Fourier-difference synthesis, and all the non-hydrogen atoms were refined anisotropically on F^2 using the full-matrix least-squares technique using the SHELXL-2018 crystallographic software package. The details of crystal parameters, data collection and refinements for **Ag-MOF1** and **Ag-MOF2** are listed in Table 1, and the selected bond lengths and angles are given in Table S1.

Product quantification

The possible gas products (H$_2$, CO, CH$_4$, C$_2$H$_4$) were directly vented into the gas chromatograph system (GC 9790II, Fuli) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) with a methanizer. The possible liquid products were quantified by ^{1}H NMR spectroscopy (Bruker-DRX 500 MHz) using dimethyl sulfoxide (DMSO) as an internal standard. The pre-saturation method was used to suppress the water peak.

The FE was calculated using the following equations:

$$FE_{gas} = \frac{n \times F \times p \times V_{gas} \times q_{gas}}{i \times R \times T} \times 100\%$$

where n is the number of transferred electrons for products, $p = 101.3$ kPa, V_{gas} is the concentration of gas product detected by GC, F is the Faraday constant, $T = 298.15$ K, q_{gas} is the gas flow rate (20 mL min^{-1}), R is the gas constant, i is the total current density.

Table S1. Selected bond lengths (Å) and angles (°) for **Ag-MOF1** and **Ag-MOF2**.

Ag-MOF1			
Ag(1)-O(1)	2.5898(14)	Ag(1)-N(1)	2.314(9)
Ag(1)-N(1)#1	2.314(9)	Ag(1)-N(1)#2	2.314(9)
O(1)-Ag(1)-N(1)#1	112.1(2)	O(1)-Ag(1)-N(1)#2	112.1(2)
O(1)-Ag(1)-N(1)	112.1(2)	N(1)#1-Ag(1)-N(1)#2	106.8(2)
N(1)#1-Ag(1)-N(1)	106.8(2)	N(1)-Ag(1)-N(1)#2	106.8(2)
Ag(1)-O(1)-Ag(1)#3	109.5	Ag(1)-O(1)-Ag(1)#4	109.5
Ag(1)#4-O(1)-Ag(1)#3	109.5	Ag(1)#5-O(1)-Ag(1)#3	109.5
Ag(1)-O(1)-Ag(1)#5	109.471(1)	Ag(1)#4-O(1)-Ag(1)#5	109.471(1)
C(1)-N(1)-Ag(1)	130.5(7)	C(3)-N(1)-Ag(1)	120.1(7)

Symmetry transformations used to generate equivalent atoms: #1 1-Y,1-Z,+X;

#2 +Y,1-Z,1-X; #3 +Y,1-Z,1-X; #4 1-Z,+X,1-Y; #5 1-Y,1-X,+Z;

Ag-MOF2			
Ag(1)-N(1)#1	2.119(5)	N(1)-Ag(1)-N(1)#1	180.0
C(1)-N(1)-Ag(1)	126.2(4)		

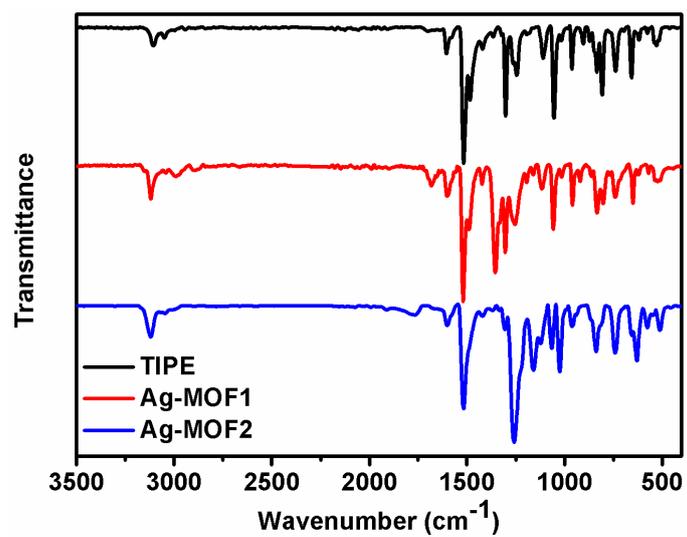Symmetry transformations used to generate equivalent atoms: #1 3/2-X,3/2-Y,1-Z;
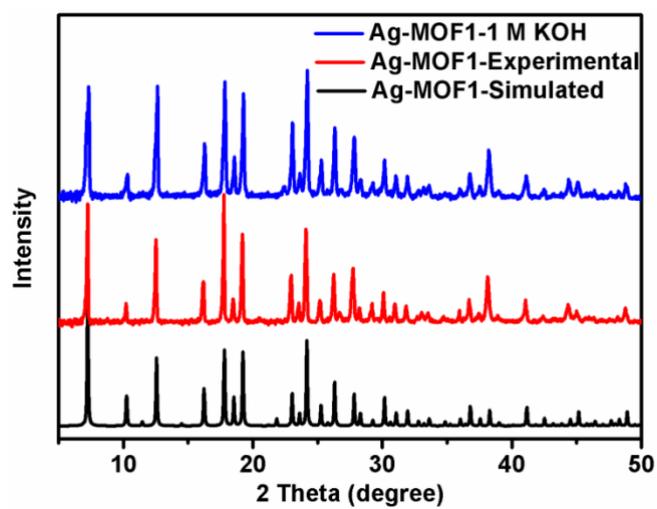
Fig. S1 FT-IR spectra of TIPE, **Ag-MOF1** and **Ag-MOF2.**
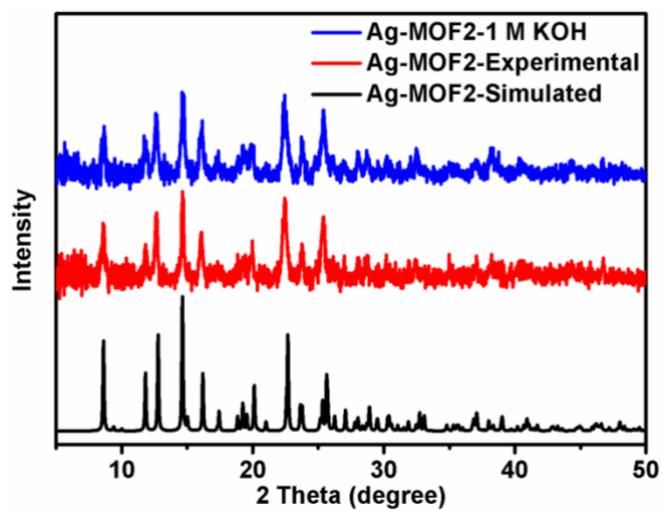

Fig. S2 PXRD patterns of **Ag-MOF1**.

Fig. S3 PXRD patterns of **Ag-MOF2**.
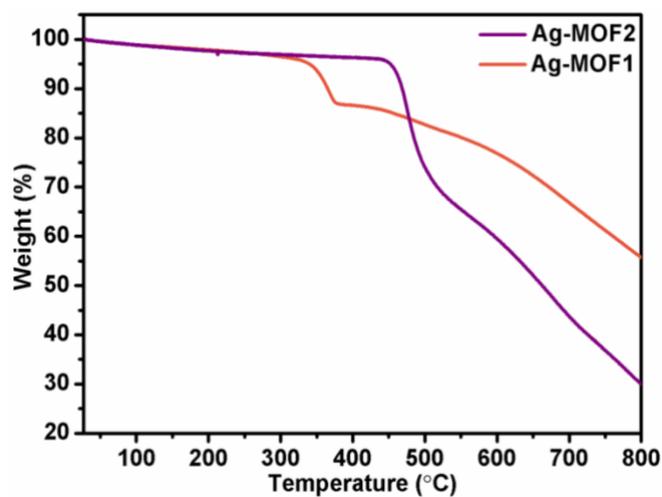
Fig. S4 TG curves of **Ag-MOF1** and **Ag-MOF2**.
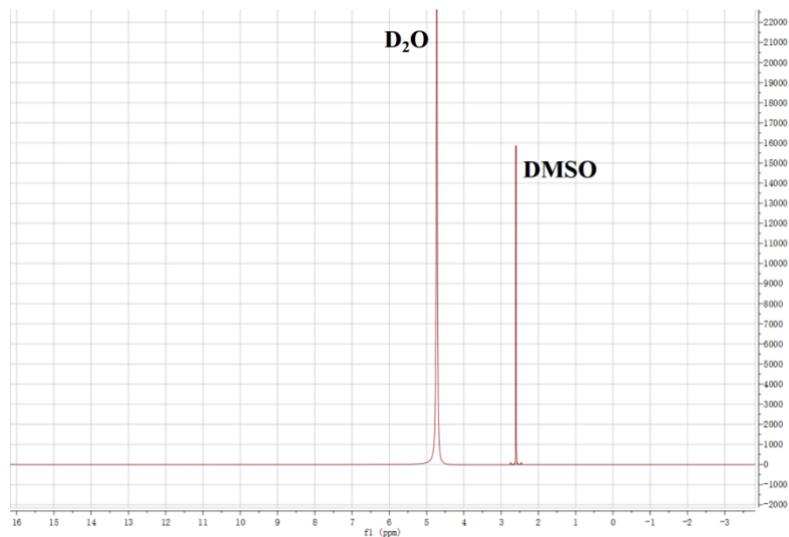
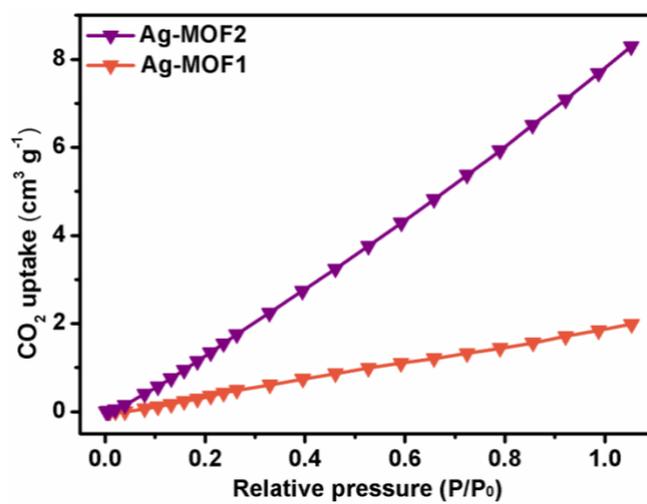**Fig. S5** ^1H NMR spectrum of electrolyte after CO_2RR.

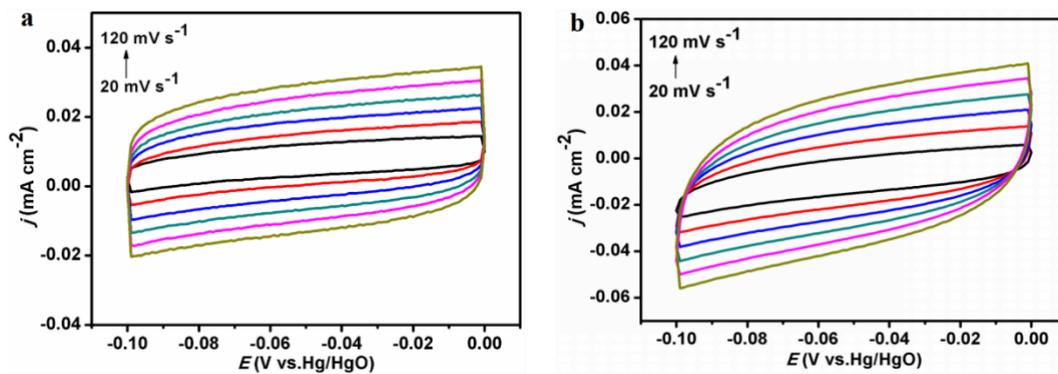**Fig. S6** CO_2 adsorption isotherms of **Ag-MOF1** and **Ag-MOF2** at 273 K.

Fig. S7 Cyclic voltammograms in the range of -0.1 to 0 V vs. Hg/HgO with different scan rates of 20, 40, 60, 80, 100 and 120 mV s^{-1} for (a) **Ag-MOF1** and (b) **Ag-MOF2**.
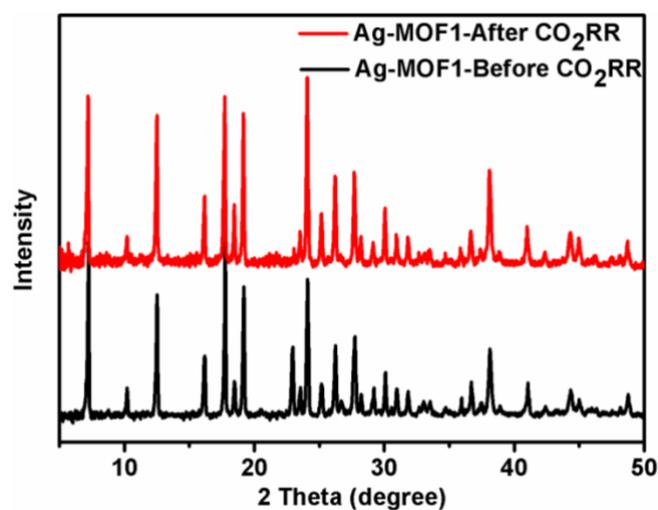

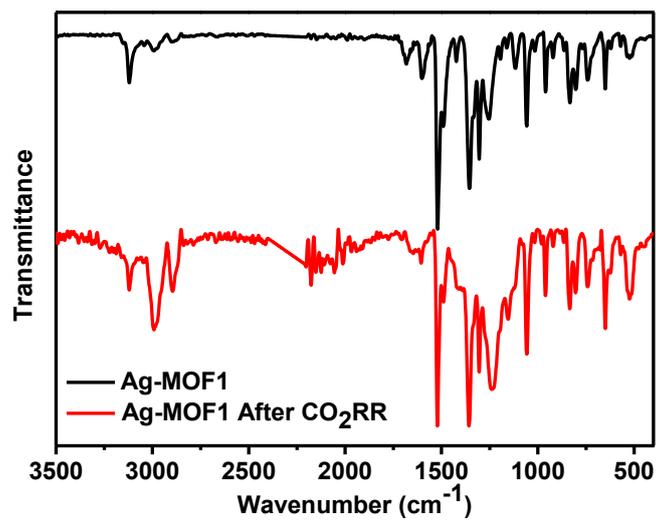**Fig. S8** PXRD patterns of **Ag-MOF1** before and after CO$_2$RR test.

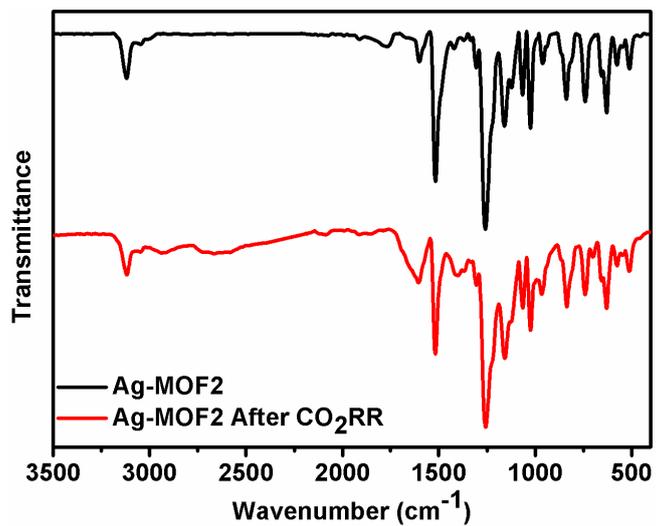**Fig. S9** FT-IR spectra of **Ag-MOF1** before and after CO₂RR test.

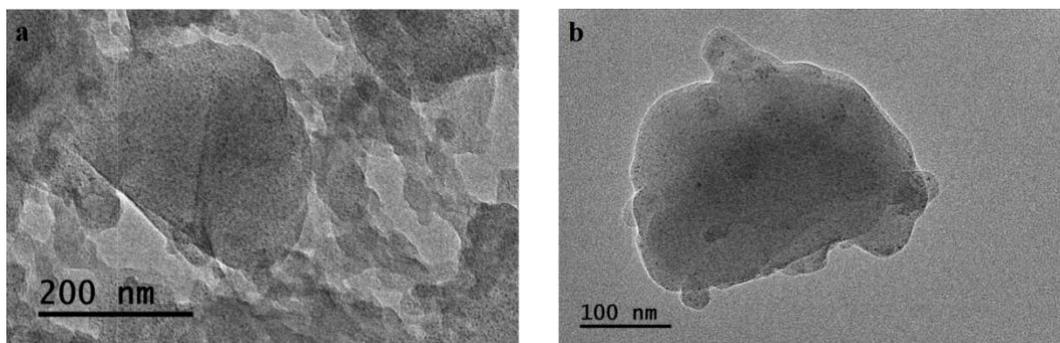**Fig. S10** FT-IR spectra of **Ag-MOF2** before and after CO₂RR test.

Fig. S11 TEM of (a) **Ag-MOF1** and (b) **Ag-MOF2**.

Table S2. Comparison the selectivity and partial current density of CO production with reported catalysts.

Catalysts	Electrolyte	FE$_{CO}$ (%)	Partial Current Density of CO (mA cm^{-2})	Ref.
Ag-MOF1	**1 M KOH**	**78.02**	**28.45**	**this work**
Ag-MOF2	**1 M KOH**	**92.21**	**29.51**	**this work**
Fe-PMOF	0.5 M KHCO$_3$	29.0	4.9	[2]
Ni-PMOF	0.5 M KHCO$_3$	19.0	3.2	[2]
Co-PMOF	0.5 M KHCO$_3$	99.0	19.5	[2]
[Al$_2$(OH)$_2$(Co(tcpp))]	0.5 M KHCO$_3$	76	1.0	[3]
Fe-MOF-525	1 M tbaPF$_6$ in CH$_3$CN	60	2.3	[4]
ZIF-8	0.5 M NaCl	65	~3	[5]
PCN-222-Fe	0.5 M KHCO$_3$	91.0	1.2	[6]
{Ag$_{49}$Mo$_{16}$}	0.5 M KHCO$_3$	44.75	~10	[7]

References

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