Supporting Information for

A large π-conjugated ligand in metal-organic framework as opticalswitch to regulate the electron transfer pathway for highly selective reduction of CO_2 to CH_4

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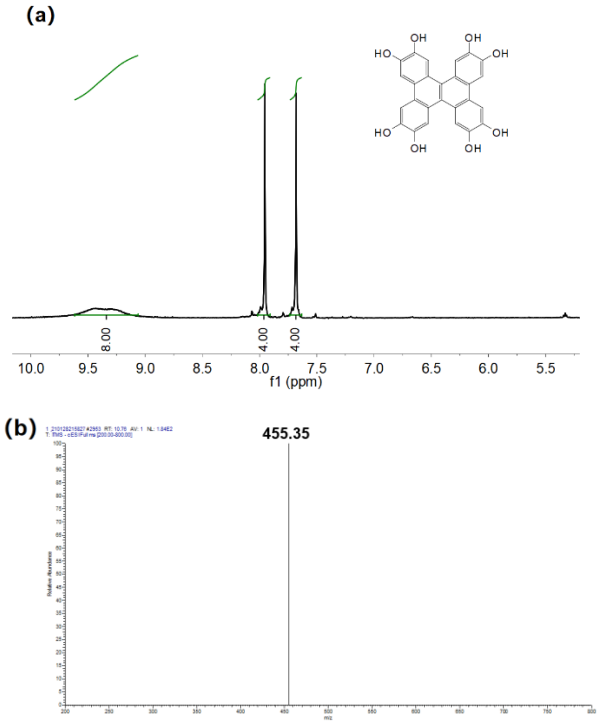

Figure S1. (a-b) ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrum and mass spectrum of H_8dbc. ^{1}H NMR (400 MHz, DMSO) δ (ppm): 7.68(s, 4H), 7.95 (s, 4H) and 9.37 (s,8H). The successful synthesis of H8DBC were demonstrated by the ^{1}H NMR spectrum and Mass spectrum.

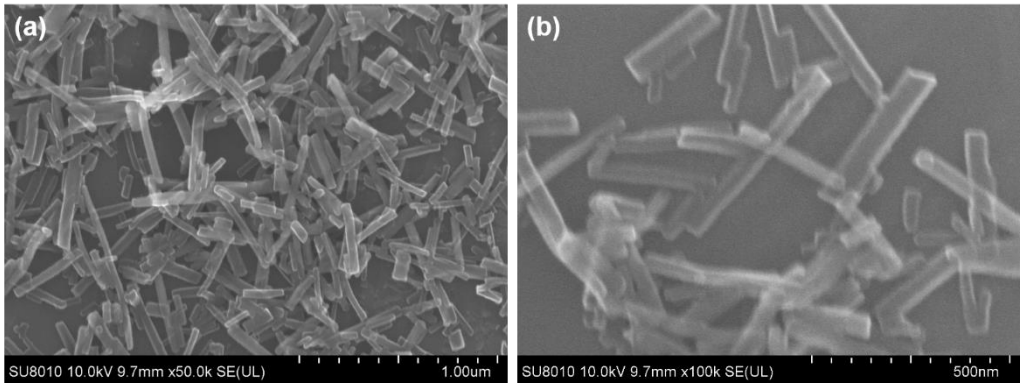

Figure S2. (a-b) SEM images of **Cu-DBC**.

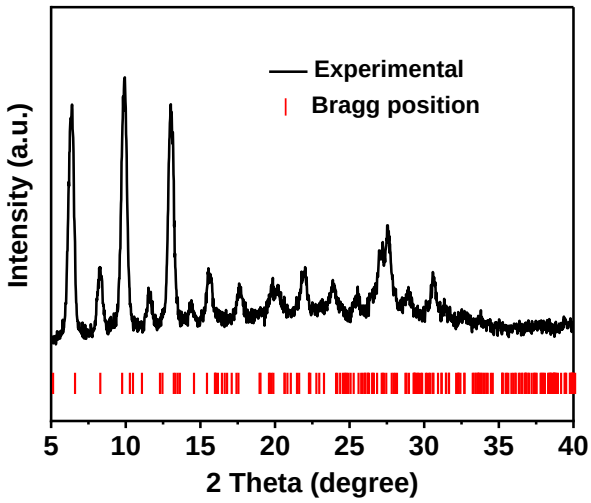

Figure S3. PXRD pattern of **Cu-DBC**.

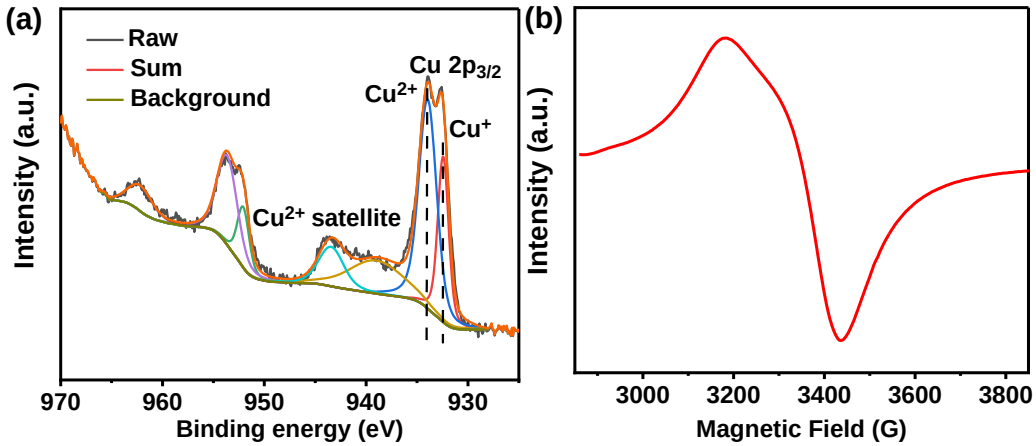

Figure S4. (a) Cu 2p XPS spectrum of **Cu-DBC**. (b) EPR spectrum of solid **Cu-DBC**.

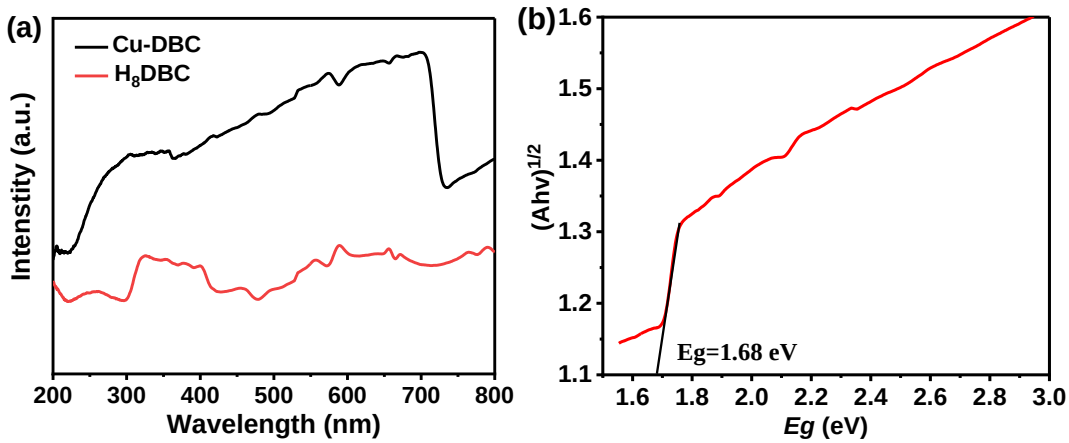

Figure S5. (a) UV-vis diffuse reflectance spectra of **Cu-DBC** and H_8dbc. (b) The Tauc plot of **Cu-DBC**.

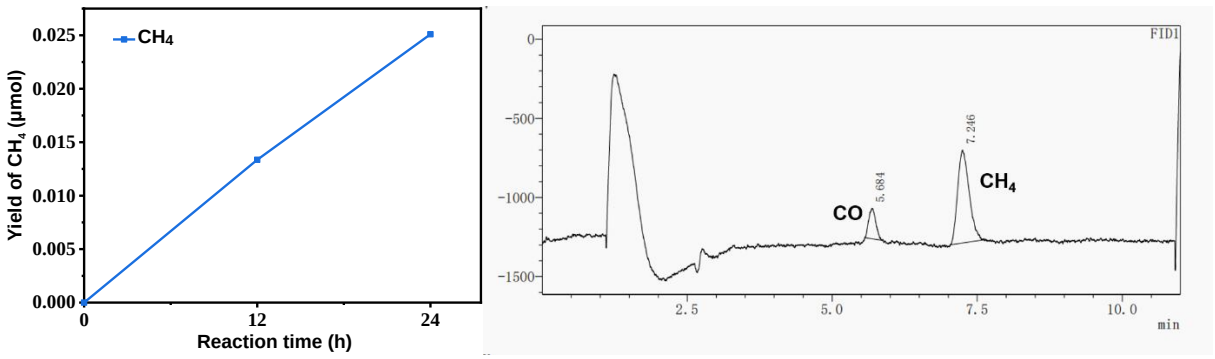

Figure S6. CH_4 production rate of photocatalytic CO_2 reduction by **Cu-DBC** (left) and GC spectrum of photocatalytic production (right) and n(CH_4) = 0.025 μmol, n(CO) = 3.08×10^{-5} μmol. Reaction condition: catalyst (1 mg), solvent (5 mL, CH_3CN/H_2O = 4:1), triethanolamine (TEOA, 0.1 mol), LED light (λ = 420 nm), 1.0 atm (pure CO_2).

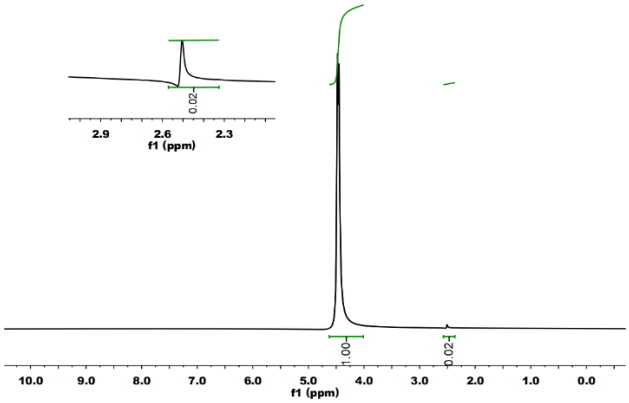

Figure S7. The ^1H nuclear magnetic resonance (^1H NMR) spectrum of the liquid phase in electrocatalytic CO_2 reduction.

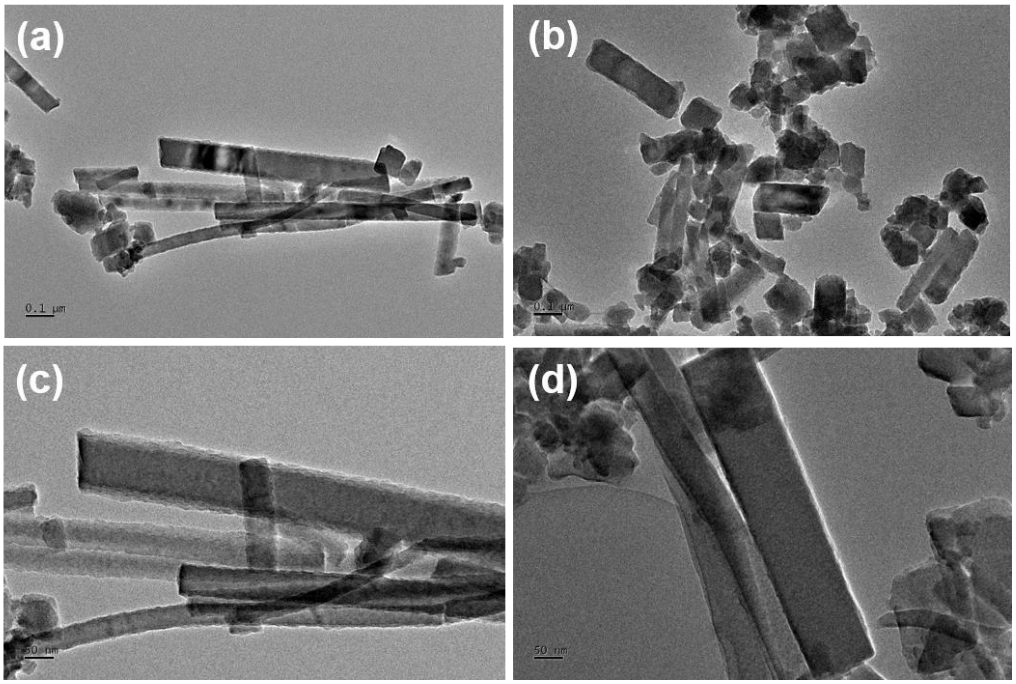

Figure S8. (a, c) TEM images of **Cu-DBC**. (b, d) TEM images of **Cu-DBC** after CO_2 reduction at -1.4 V *vs*. RHE for 2.5 h.

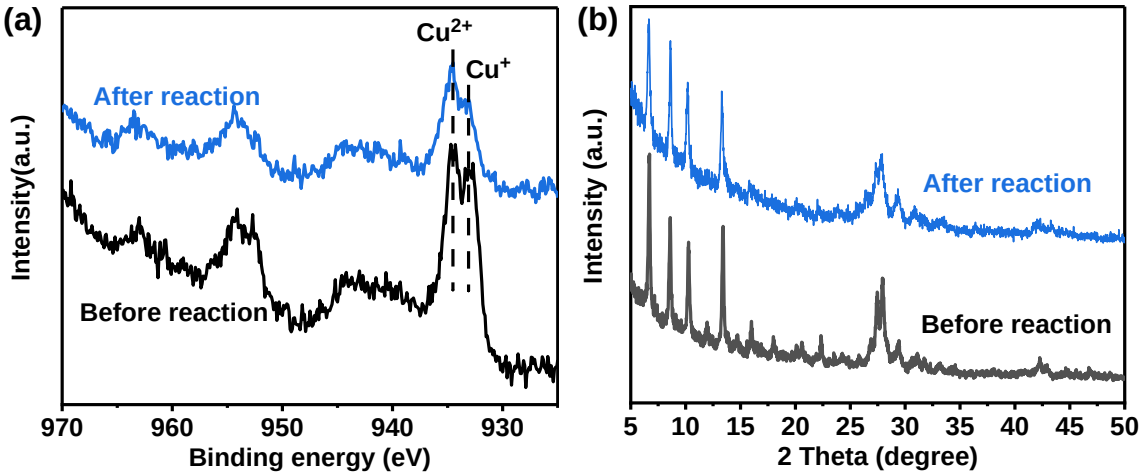

Figure S9. (a-b) Cu 2p XPS spectra and PXRD patterns of **Cu-DBC** before and after CO_2 reduction at -1.4 V *vs*. RHE for 2.5 h.

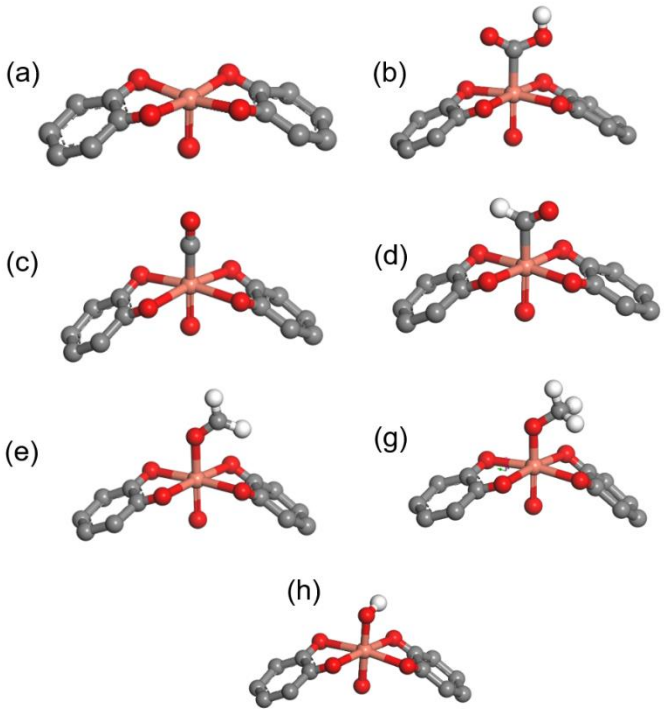

Figure S10. Illustration of intermediates in electrocatalytic CO_2RR, which represent * (a), *COOH (b), *CO (c), *CHO (d), * OCH_2 (e), *OCH_3 (f), and *OH (g) intermediates.

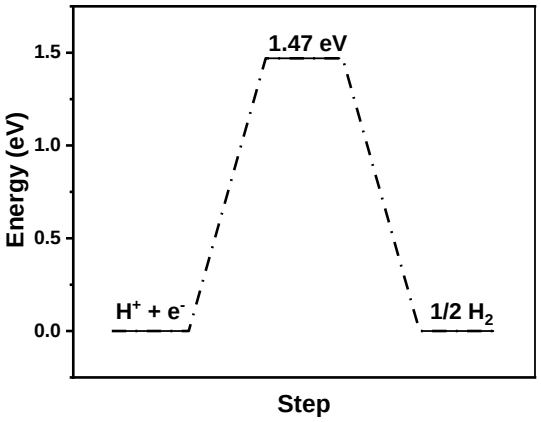

Figure S11. Illustration of the energy barrier of hydrogen evolution reaction of **Cu-DBC**.

Table S1. Summary of the reported systems of photo-coupled electrocatalytic and electrocatalytic CO_2 reduction.

Catalyst	Electrocatalyst	Electrolyte	Main product	Potential	FE	Reference
PECR catalyst	**Cu-DBC**	**0.1 M $KHCO_3$**	**CH_4**	**-1.0 V**	**84.3%**	**This work**
				-1.2 V	**88.6%**	
				-1.4 V	**93.2%**	
	Ag-supported dendritic Cu	0.1 M $CsHCO_3$	Hydrocarbons	-1.0 V *vs* SCE	79 ±6%	2
	Porphyrin-Au	0.1 M $KHCO_3$	CO	-0.9 V	94%	3
	CoPc-Rs/Fe_2O_3 NTs	0.1 M $KHCO_3$	CH_3OH	-1.3V	84%	4
	NiPc-TFPN COF	0.5 M $KHCO_3$	CO	-0.9 V	99%	5
	GaN:Sn	0.1 M $KHCO_3$	HCOOH	-0.53 V	76%	6
	FeS_2 /TiO_2 NTs	0.1 M $KHCO_3$	CH_3OH	-1.2 V.SCE	39.8%	7
Electrocatalysts	FN-CTF-400	0.1 M $KHCO_3$	CH_4	-0.7 ~ -0.9 V	99.3%	8
	Cu/MoS_2	0.1 M $NaHCO_3$	CO	-0.8 V	35.2%	9
	CuO_x nanoparticle	0.1 M $KHCO_3$	C_2H_4	-1.0 V	21%	10
	Cu_2O@CuHHTP	0.1 M KCl/0.1 M $KHCO_3$	CH_4	-1.4 V	73%	11
	Cu phthalocyanine	0.5 M $KHCO_3$	CH_4	-1.06 V	66%	12
	Pd/Cu_2O-Cu	0.5 M $NaHCO_3$	CH_4	-0.65 V	30%	13

Notes: The potentials mentioned in this table are based on the reversible hydrogen electrode (RHE) unless otherwise stated. All the reported electrocatalysts at the listed potentials exhibited maximum product selectivity.

Experimental section

Materials and general methods. The ligand dibenzo-[g,p]chrysene-2,3,6,7,10,11,14,15-octaol was synthesized according to the literature[1] Other reagents were commercially available and without further purification. Power X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer (Cu Kα). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer. A SU8010 scanning electron microscope was utilized to investigate the morphology of Cu-DBC. High resolution images of microcrystalline powder of Cu-DBC before and after CO_2 reduction reaction were obtained by a transmission electron microscope (TEM). ^{1}H Nuclear magnetic resonance (^{1}H NMR) measurements were performed on a Bruker advance III. Attenuated total reflection infrared (ATR-FTIR) spectra were recorded on a Nicolet 6700 (Thermo Fisher) to study the reaction intimidates formed over Cu-DBC in the electrochemical measurements.

Synthesis of Cu-DBC. dibenzo-[*g*,*p*]chrysene-2,3,6,7,10,11,14,15-octaol (8.6 mg) and $Cu(OAc)_2$ (6 mg) were dissolved in 500 μL DMF and 2 mL deionized water. After ultrasonic treatment for 30 minutes, the vessel was placed in an oven with the temperature of 85 ℃ for 72 hours. Then the MOF was separated from the reaction mixtures by washing with water and dried overnight in 60 ℃ to obtain the black product.

Photochemical experiments: Cu-DBC (1 mg) was dispersed in a mixed solution (5 ml, CH_3CN/H_2O = 4:1), with ultrasonication for 30 min. The suspension was added 0.1 mol triethanolamine (TEOA), and then purged by CO_2 gas at a pressure of 1 atm for 30 min. The reaction mixture was continuously stirred with a magneton and irradiated under a LED light with a wavelength of 420 nm. The reaction gaseous products were analyzed by a gas chromatography (Agilent 7890B).

Electrocatalytic CO_2 reduction. All the electrochemical measurements were conducted with a CHI660E chemical workstation and the H-type cell was used as the electrolyzer for electrocatalytic CO_2 reduction. The preparation methods of working electrode is as follows: Cu-DBC (5 mg) was dispersed in 500 μL isopropanol and 50 μL Nafion (5wt%) by ultrasonic treatment for 30 minutes to achieve a homogenous catalyst ink. Then 50 μL catalyst ink was dropped uniformly onto the conductive fluorine-doped tin oxide (FTO) substrate, furnishing the working electrode. Detailly,

Cu-DBC/FTO, Pt wire, and Ag/AgCl were used as working electrode, counter electrode and reference electrode to form a three-electrode system. All the electrode potentials were measured against a Ag/AgCl electrode and converted to reversible hydrogen electrode (RHE) based on the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.197\,V + 0.059 \times pH$$

A 0.1 M $KHCO_3$ aqueous solution was used as the electrolyte and the pH value for 0.1 M CO_2-satured $KHCO_3$ solution is 6.8. Before the electrochemical measurements, high purity of CO_2 was purged into the H-type cell for 30 minutes at a flow rate of 20 ml/min. The reaction products were injected every 20 minutes and monitored by a gas chromatography (Agilent 7890B) equipped with flame ionization detector (FID), and thermal conductivity detector (TCD). Specifically, H_2 was detected by TCD, and CH_4, C_2H_4 and CO were detected by FID. The Faradaic efficiency of gas products were calculated by the equation:

$$FE = \frac{PV}{T} \times \frac{vNF}{I}$$

In which, FE represents the faradaic efficiency for CH_4, CO, H_2 or C_2H_4; P, V and T means the reaction pressure (1 atm), gas flow rate (20 ml/min) and reaction temperature (298.15 K), respectively; F and *v* represent Faradaic constant (96485 C/mol) and volume ratio of different gas products in the outlet gas from the electrolyzer; N and I represent the electron transfer number, which is 8 for CH_4, 2 is for H_2 or CO, and current, respectively.

Photo-coupled electrochemical CO_2 reduction measurements. The photo-coupled electrochemical measurements were similar with the measurements of electrochemical measurements. All the measurements were carried out in an H-type cell with a quartz window, using a Cu-DBC/FTO working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The working electrode was irradiated through the quartz window, under a 300 W Xe lamp, with a light intensity of 300 mW cm^{-2}, and irradiated area of 1 cm^2. The recorded potentials were converted to vs RHE, which were identical to that of electrochemical measurements. The detection of gas products was carried out on an online gas chromatography analytical instrument (Agilent 7890B).

Photocurrent response of Cu-DBC. The microcrystalline powder of Cu-DBC was coated on FTO substrate with Nafion binder to prepare the working electrode. The photo-responsive signals were measured under chopped light at the potential of -1.0 V *vs*. Ag/AgCl in a CO_2-saturated 0.1 M Na_2SO_4 solution.

Mott-Schottky measurements. The Mott-Schottky measurements were conducted with a CHI660E chemical workstation at different frequencies (500 Hz, 1000 Hz and 1500 Hz) and in an electrolyzer with a quartz window, using a Cu-DBC/FTO working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. A 0.1 M Na_2SO_4 solution was used as the electrolyte.

Computational methods. All calculations were performed on Materials studio 5.5 package. The potential energy surfaces for CO_2RR catalyzed by Cu-DBC were calculated through the periodic density functional theory (PDFT) method by the $Dmol^3$ module. The widely used generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and TS for DFT-D correction were involved.

Supplementary References

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