Electronic Supplementary Information (ESI) for

Covalently Anchoring Cobalt Phthalocyanine on Zeolitic Imidazolate Frameworks for Efficient Carbon Dioxide Electroreduction

Zhongjie Yang,[a,b] Xiaofei Zhang,[a] Chang Long,[a,c] Shuhao Yan,[a] Yanan Shi,[a] Jianyu Han,[a] Jing Zhang,[d] Pengfei An,[d] Lin Chang,[a,b] and Zhiyong Tang*[a,b]

[a]*CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.*

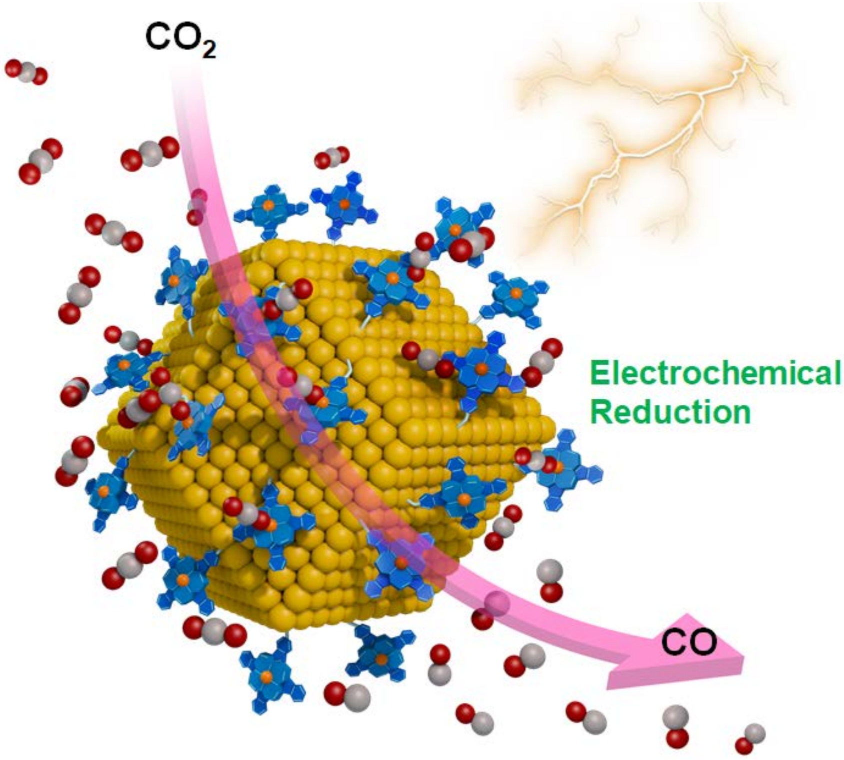
[b]*University of Chinese Academy of Sciences, Beijing 100049, China.*

[c]*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150080, China.*

[d]*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R. China.*

E-mail: zytang@nanoctr.cn

Table of Contents:



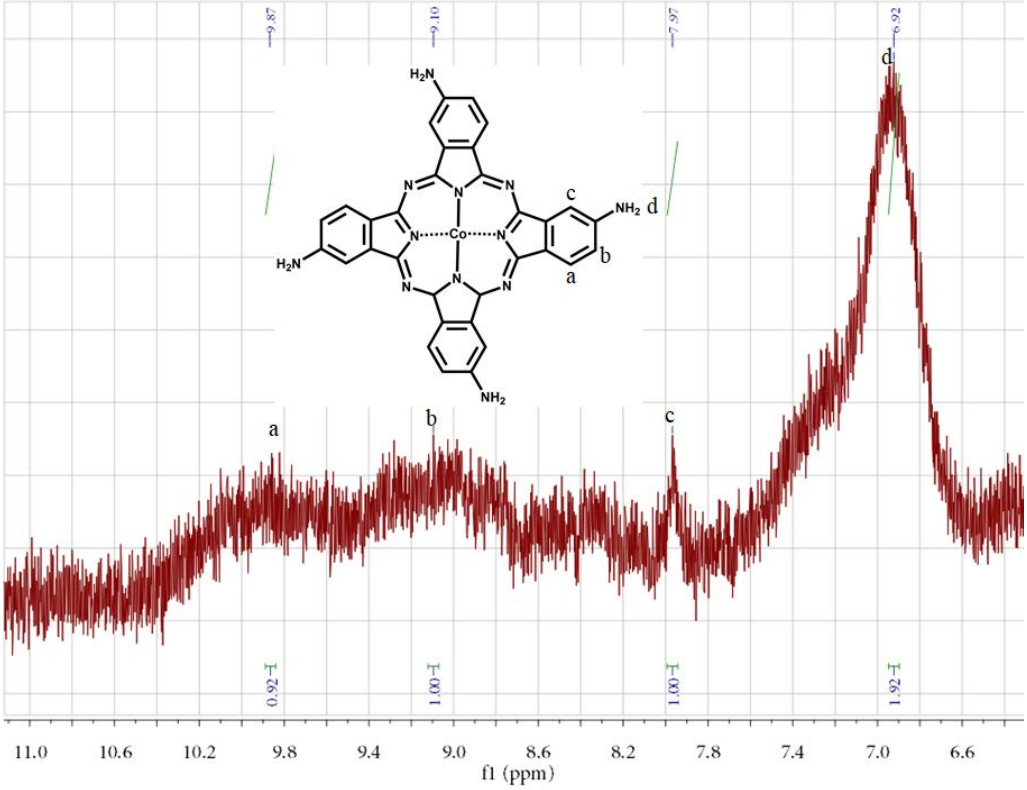


Figure S1. ^1H NMR spectrum of cobalt tetrraaminophthalocyanine.

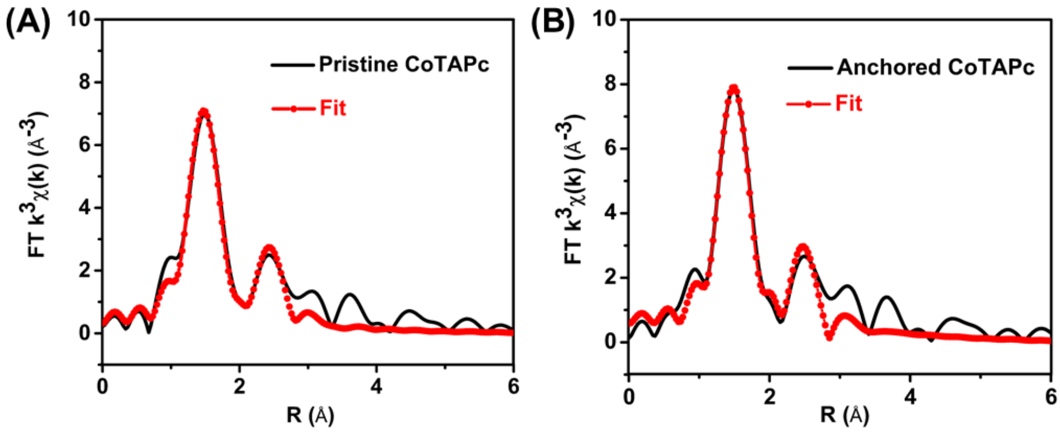


Figure S2. (A) *Ex situ* EXAFS data (solid curve) in *R* space and best fitting result (circled curve) of pristine CoTAPc. (A) *Ex situ* EXAFS data (solid curve) in *R* space and best fitting result (circled curve) of anchored CoTAPc.

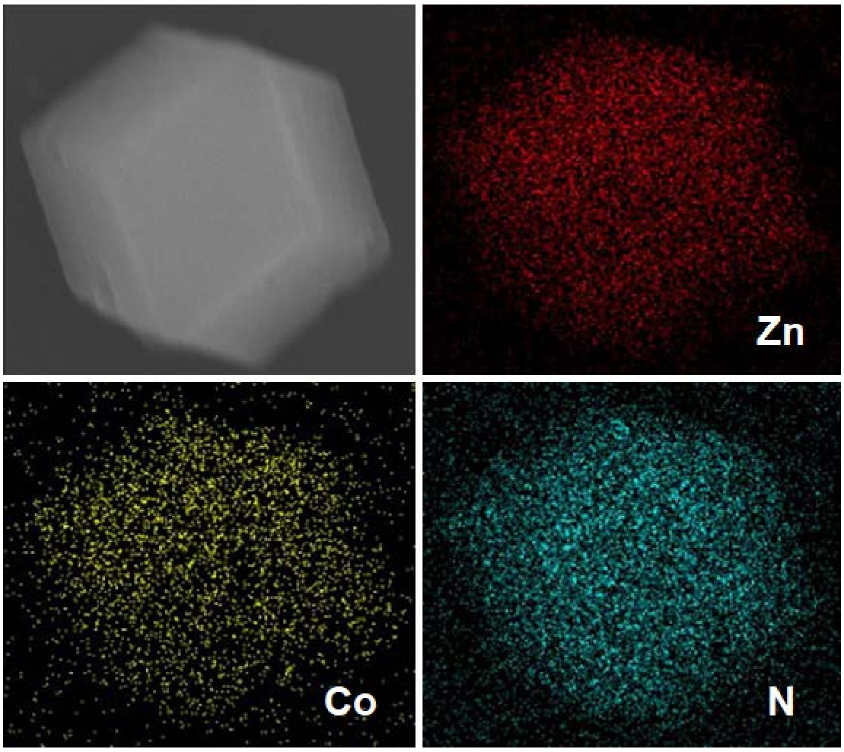


Figure S3. Energy dispersive X-Ray spectroscopy (EDS) mapping images of ZIF-90-4.

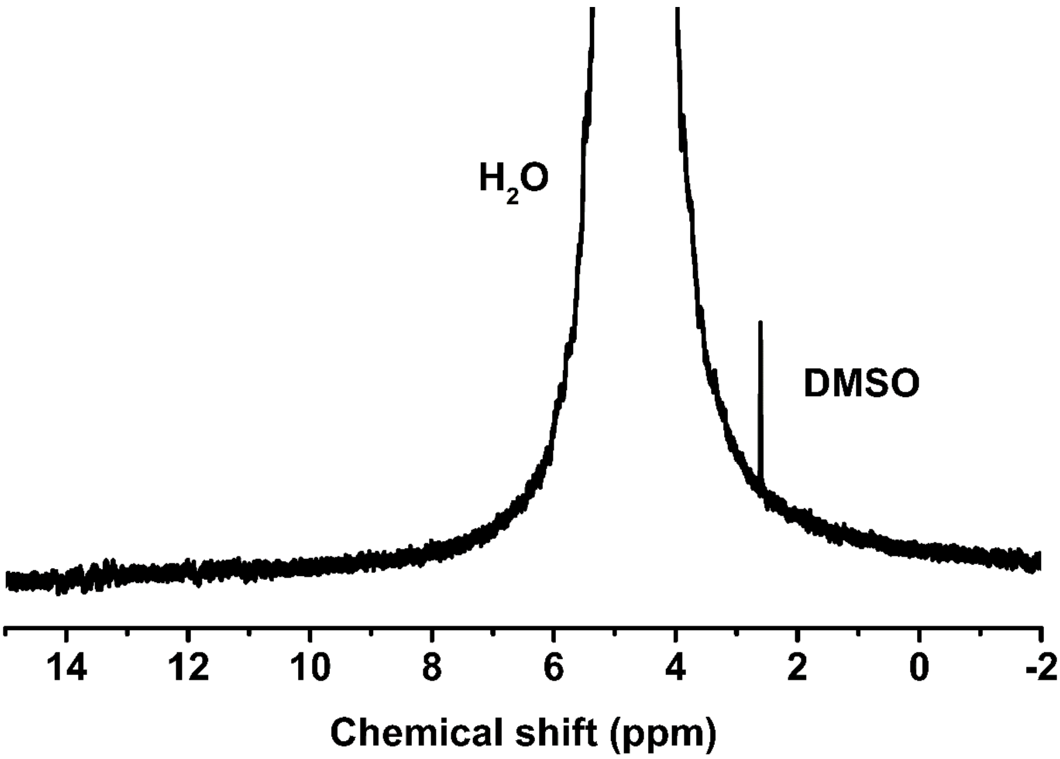


Figure S4. Representative NMR spectrum of the electrolyte after CO_2 reduction at−0.97 V *vs.* RHE. DMSO is used as an internal standard for quantification of liquid products.

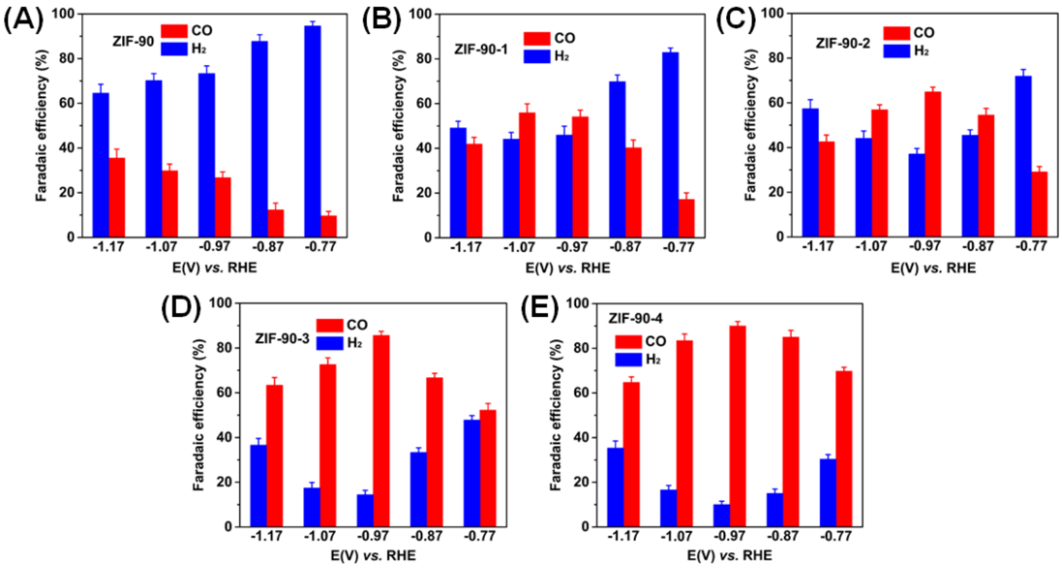


Figure S5 A-E. CO and H_2 Faradaic efficiency for ZIF-90, ZIF-90-1, ZIF-90-2, ZIF-90-3 and ZIF-90-4 at different applied potentials.

During 2 h electrolysis, 0.5 M $NaHCO_3$ aqueous solution electrolyte at the cathodic part was under continuously mild stir and bubbled with CO_2 at the speed of 20 mL/min.

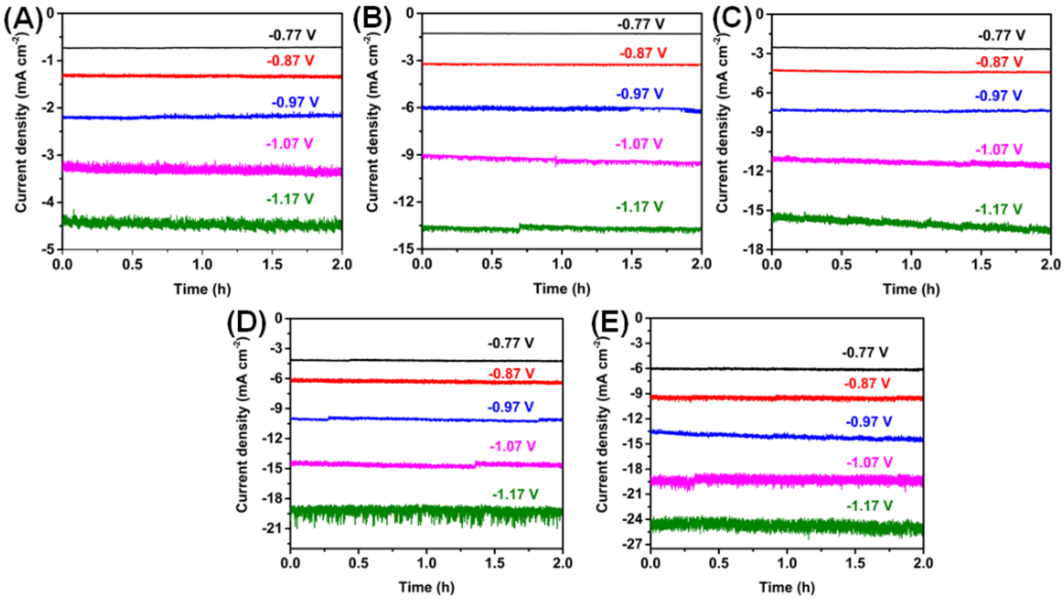


Figure S6 A-E. Chronoamperometric curves of ZIF-90, ZIF-90-1, ZIF-90-2, ZIF-90-3 and ZIF-90-4 at different applied potentials as indicated.

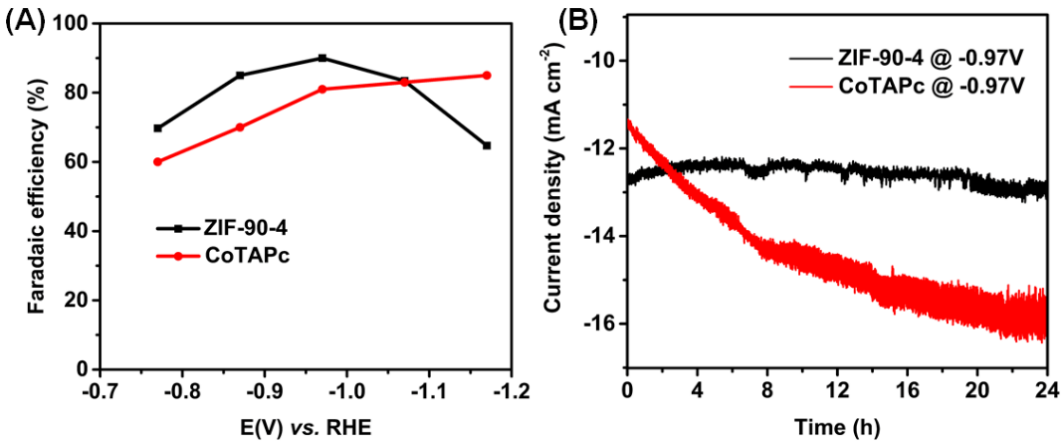


Figure S7. (A). Faradaic efficiency of CO for CoTAPc and ZIF-90-4 (B). Chronoamperograms of CoTAPc and ZIF-90-4 over 24 h at -0.97 V *vs.* RHE.

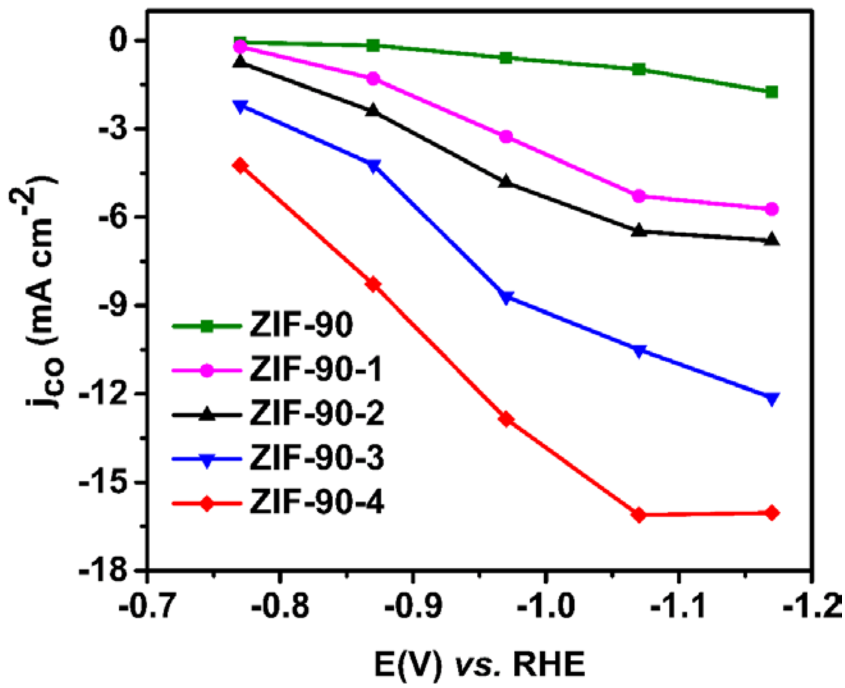


Figure S8. Partial CO current density of ZIF-90, ZIF-90-1, ZIF-90-2, ZIF-90-3 and ZIF-90-4.

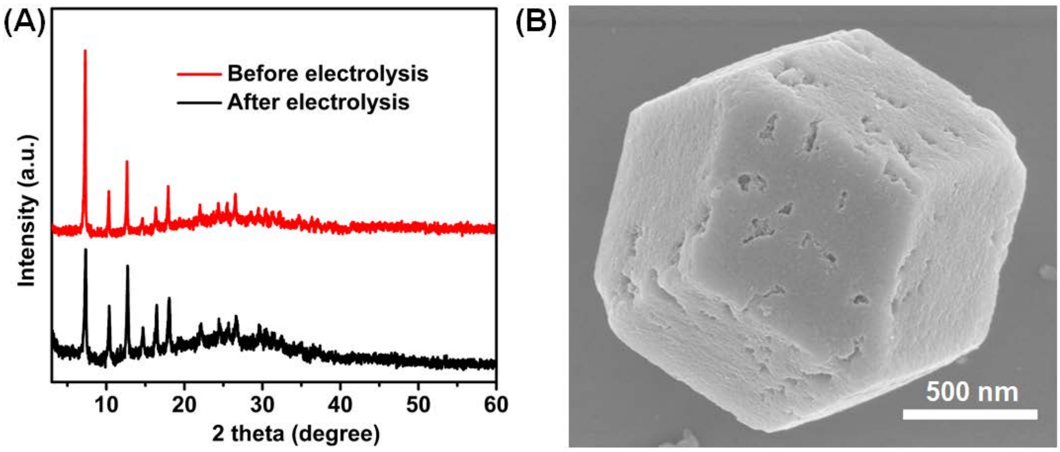


Figure S9. (A) PXRD patterns of ZIF-90-4 before and after electrolysis. (B) SEM image of ZIF-90-4 after electrolysis. The crystal structure of ZIF-90-4 after 48 h electrocatalysis at a given potential of -0.97 V keeps unchanged. The dodecahedron morphology is well maintained after 48 h electrocatalytic electrolysis at a given potential of -0.97 V.

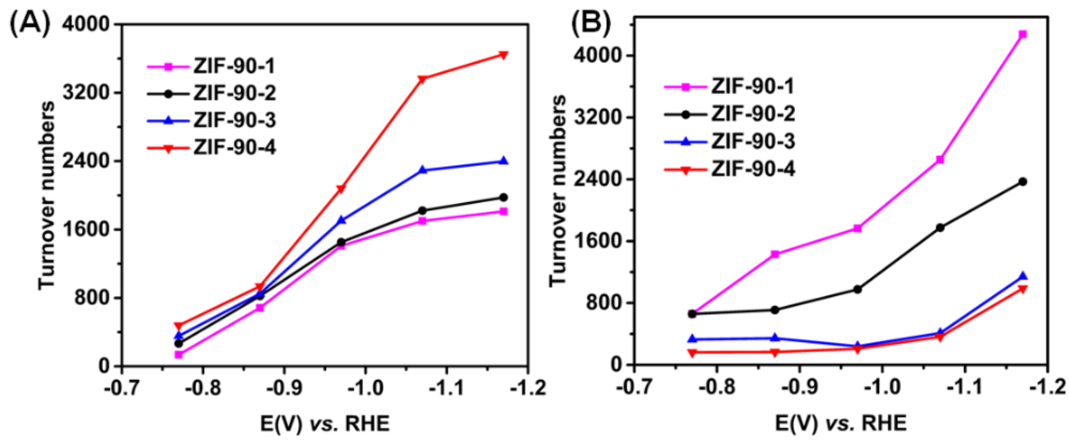


Figure S10 (A). The CO and (B) H_2 TONs of ZIF-90-1, ZIF-90-2, ZIF-90-3 and ZIF-90-4 at different applied potentials for 2 h electrolysis.

Table S1. Calculated and experimental Co element content in CoTAPc-ZIF-90.

Samples	ZIF-90-1	ZIF-90-2	ZIF-90-3	ZIF-90-4
Experimental Co (wt.%)	0.46	0.83	1.81	2.61
Calculated Co (wt.%)	0.44	0.88	1.76	2.64
After electrolysis Co (wt.%)	0.39	0.81	1.68	2.59

Table S2. Fitting parameters of Co K-edge EXAFS curves for pristine CoTAPc and anchored CoTACo.

Samples	Path	C.N.	R (Å)	$\sigma^2 \times 10^3$ (Å^2)	ΔE (eV)	R factor
Pristine CoTAPc	Co-N	3.7±0.9	1.92±0.01	3.4±1.8	3.2±3.4	0.007
	Co-C	4.5±2.7	2.93±0.03	8.0±4.6	5.2±4.9	
Anchored CoTACo	Co-N	4.0±0.7	1.91±0.01	2.4±1.	7.4±2.7	0.006
	Co-C	4.3±2.4	2.94±0.03	7.8±4.5	9.2±4.0	

*S_0^2 = 0.9

Method: Calculation of turnover numbers

Turnover number (TON) is defined as the mole of reduction product generated per electrocatalytic active site over a given period of time. In this work, bulk electrocatalysis was performed at different applied potentials for 2 h.

The total amount of Co in ZIF-90-4 was calculated as follows:

$$n_{Tot} = \frac{mw_{Co}}{A} = \frac{0.75\ \ mg \times 2.61\%}{58.93\ \ g/mol} = 3.32 \times 10^{-7} mol$$

where n_{Tot} was the total amount of Co on the working electrode, m was the mass of the hybrid electrocatalyst loaded on the working electrode, w_{Co} was the weight fraction of Co in the hybrid electrocatalyst determined from the ICP analysis, and A was the atomic weight of Co.

The calculation of TONs:

$$TONs = \frac{i_{Tot \times FE_{product}} \times t}{2F \times n_{Tot}}$$

Where i_{Tot} was the total current, $FE_{product}$ was the Faradaic efficiency of CO and H_2, t was the electrolysis time, and F was the Faradaic constant.

We took the calculation of TONs at -0.97 V for 2 h electrolysis for ZIF-90-4 as an example. The recorded total current was 14.28 mA (Figure S 6E). TONs were calculated by assuming that all Co sites were involved in CO_2RR electrocatalysis:

$$TONs = \frac{i_{Tot \times FE_{CO}} \times t}{2F \times n_{Tot}} = \frac{14.28\ \ mA \times 90\% \times 7200\ \ s}{2 \times 96485 C/mol \times 3.32 \times 10^{-7} mol} = 1946$$