

Supplementary Information

Three Dimensional Cyclic Trinuclear Units Based Metal-Covalent Organic Frameworks for Electrochemical CO₂RR

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Section S1. Materials and characterization

S1.1 Materials and General Methods

All reagents and solvents were obtained from commercial suppliers and used without further purification (Sigma-Aldrich, TCI, J&K Scientific LTD). The powder X-ray diffraction (PXRD) data were measured on a PANalytical B.V. Empyrean powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over the range of $2\theta = 2.0\text{--}40.0^\circ$ with a step size of 0.02° . Thermogravimetric curves were obtained using a SHIMADZU DTG-60 thermal analyzer under N₂ atmosphere with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The operational range was from 30°C to 800°C . Solid-state ¹³C NMR spectra were determined on an AVIII 400 MHz solid-state NMR spectrometer. FT-IR spectra (KBr) were recorded by using a SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer. Data of Brunauer-Emmer-Teller (BET) surface area and porosity were collected by using a **B**SD-PS Specific Surface area & Pore Size Analyzer at 77 K. Before gas adsorption measurement, and the samples were washed by acetone three times ($3 \times 5.0 \text{ ml}$) and the acetone was extracted under vacuum at 85°C to provide the sample for sorption analysis. X-ray photoelectron spectroscopy was operated on Thermo Scientific ESCALAB 250 Xi X-ray photoelectron spectrometer. JEM-2100 transmission electron microscopy was applied for TEM images, and the scanning electron microscopy (SEM) images were obtained on JEOL JSM-6700 scanning electron microscope. ICP analysis was carried out on an Ultima 2 analyzer. Electrochemical CO₂RR measurements were performed in a three-electrode H-type cell with an electrochemical station (CHI 660E). CO₂ (99.999%) was purchased from Xinhang Gas (Fuzhou, China). The gas products were analyzed by gas chromatography (9790II FULI), and liquid products were detected by gas chromatography (9720 FULI). Formic acid was detected by an ion chromatograph (CIC-D100).

S1.2 The synthesis of 3D-CTU-MCOF

Synthesis of Cu₃L

The synthesis of Cu₃L was carried out according to the procedure described in the literature.^{S1} 1*H*-pyrazole-4-carbaldehyde (96 mg, 1.0 mmol), Cu(NO₃) \cdot 3H₂O (200 mg, 0.83 mmol), *N,N*-dimethylformamide (6.7 ml), H₂O (5.0 ml) and ethanol (6.7 ml) were added to a 25

ml Teflon-lined reactor. The mixture was then sonicated to obtain a blue solution. The mixture was heated at 100°C for 12 h under autogenous pressure and then cooled to room temperature. Light yellow crystals were obtained and washed with water and acetone for three times, respectively. And then, the product was dried under vacuum at 120 °C for 24 h (yield: 53.6 % based on Cu). IR (KBr): $\nu = 1670\text{ cm}^{-1}$, 1535 cm^{-1} , 1418 cm^{-1} , 1203 cm^{-1} , 1045 cm^{-1} , 770 cm^{-1} , 625 cm^{-1} .

Synthesis of 3D-CTU-MCOF

A Pyrex tube measuring o.d. \times i.d. = $10 \times 8\text{ mm}^3$ was charged with Cu₃L (38 mg, 0.08 mmol) and TAA (12 mg, 0.06 mmol), 1,4-dioxane (0.5 ml), 1,3,5-mesitylene (0.5 ml) and aqueous acetic acid (6 M, 0.1 ml). And then, the tube was flash frozen at 77 K, evacuated to an internal pressure of 0.15 mmHg, and flame sealed. Upon sealing, the tube length was reduced to ca. 13 cm. Subsequently, the mixture was heated at 120°C for three days to afford yellow precipitate. The product was isolated as powders by filtration and washed with ethanol, DMF, and acetone.

S1.3 General procedures of electrochemical measurements

All electrochemical measurements were carried out with a CHI 660E electrochemical station in an H-type electrolytic cell. Moreover, the active MCOFs sample was used for electrochemical catalytic experiments. The preparation method of working electrode was as follows. The mixture of catalysts (5 mg) and carbon black (1 mg) was dispersed in isopropanol (0.9 ml), and then 5% Nafion (0.1 ml) was added. The resulting mixture was sonicated for 30 min to obtain the ink. 0.05 ml of ink was dropped onto carbon paper with a catalyst loading of 0.25 mg cm^{-2} . The Ag/AgCl electrode was used as the reference electrode, and a Pt sheet electrode ($1 \times 1\text{ cm}^2$) was used as the counter electrode in all measurements.

The electrolytic cell, separated by a Nafion 211 membrane, was filled with 0.1 M EmimBF₄ in acetonitrile (the content of H₂O: 1.23%). The electrolyte was purged with CO₂ or Ar for 30 min before electrochemical measurements. The linear sweep voltammogram (LSV) scan rate was set to 20 mV s^{-1} in $-1.0 \sim -2.4\text{ V vs. SHE}$. CO₂ was controlled to flow through the cathode compartment at a rate of 20 ml min^{-1} . CV curves of MCOFs were obtained in a potential range of $0.60 \sim 0.70\text{ V vs. SHE}$ (Cu₃L: $0.45 \sim 0.55\text{ V vs. SHE}$) and the scan rates were 10 mV s^{-1} , 20 mV s^{-1} , 30 mV s^{-1} , 40 mV s^{-1} , 50 mV s^{-1} , 60 mV s^{-1} , 70 mV s^{-1} , 80 mV s^{-1} , 90 mV s^{-1} , 100 mV s^{-1} .

Product analysis. The gas products were detected by a FULI 9790II gas chromatograph (GC) equipped with a thermal conductivity detector (for H₂) and a flame ionization detector (for CO, CH₄, C₂H₄). The products were collected after running the reaction for 800s. After repeating the test three times for each sample, the FE was calculated based on the average value.

$$FE_{H_2} = \frac{H_{2ppm} \times Q_{gas} \times 2e \times 96485}{22.4 \times i}$$

$$FE_{CO} = \frac{CO_{ppm} \times Q_{gas} \times 2e \times 96485}{22.4 \times i}$$

$$FE_{CH_4} = \frac{CH_{4ppm} \times Q_{gas} \times 8e \times 96485}{22.4 \times i}$$

$$FE_{C_2H_4} = \frac{C_2H_{4ppm} \times Q_{gas} \times 12e \times 96485}{22.4 \times i}$$

H_{2ppm}: the ppm value of H₂ in the gas mixture;

CO_{ppm}: the ppm value of CO in the gas mixture;

CH_{4ppm}: the ppm value of CH₄ in the gas mixture;

C₂H_{4ppm}: the ppm value of C₂H₄ in the gas mixture;

Q_{gas}: the gas flow rate in the reactor;

“2e”“2e”“8e”“12e”: the number of electrons to be transferred for H₂, CO, CH₄ and C₂H₄ products, respectively;

i: average current at a steady state (A);

96485: Faraday constant (C mol⁻¹);

22.4: molar volume of the gas (L mol⁻¹).

The FE of each liquid phase product can be calculated using the following equations:

$$FE (\%) = \frac{Q_{product}}{Q_{Total}} \times 100\% = \frac{n_{product} \times N \times F}{j \times t} \times 100\%$$

Where Q_{product} is the amount of electric charge required to produce a specific product, Q_{total} is the total amount of electric charge consumed, n_{product} denotes the molar mass that produces a specific product, N denotes the number of electrons that have undergone a specific reaction transfer, F denotes the Faraday constant (96485 C mol⁻¹), j denotes the total current density, and t is the electrolysis time.

MeOH and EtOH production was detected using a chromatograph (GC 9720, FULI) equipped

with an RB-INOWAX column and an FID detector. The specific formulas for FEs are as follows:

$$FE_{MeOH} = \frac{n_{MeOH} \times 6e \times 96485}{Q_{total}}$$

$$FE_{EtOH} = \frac{n_{EtOH} \times 12e \times 96485}{Q_{total}}$$

n_{MeOH} : the molar amount of methanol;

n_{EtOH} : the molar amount of ethanol;

“6e”“12e”: the number of electrons to be transferred for MeOH and EtOH products, respectively;

Q_{total} : charge number.

HCOOH production was detected using an ion chromatograph (CIC-D100, ION CHROMA TOGRAPHY, SHINE) equipped with a SUGAR SH1101 column, a UV230+ and RI detector. The specific formula for FE_{HCOOH} is as follows:

$$FE_{HCOOH} = \frac{n_{HCOOH} \times 2e \times 96485}{Q_{total}}$$

n_{HCOOH} : the molar amount of formic acid;

“2e”: the number of electrons to be transferred for HCOOH production;

Q_{total} : charge number; 96485: Faraday constant ($C \text{ mol}^{-1}$).

Table S1. $FE(C_2H_4)$, $FE(EtOH)$, $FE(CH_3OH)$, $FE(HCOOH)$, $FE(CH_4)$, $FE(CO)$ and $FE(H_2)$ of (a) 3D-CTU-MCOFs, (b) Cu_3L at several selected potentials between -1.2 ~ -2.2 V vs SHE.

Working electrode	Potential (V vs SHE)	FE (C_2H_4) (%)	FE (EtOH) (%)	FE (CH_3OH) (%)	FE (HCOOH) (%)	FE (CH_4) (%)	FE (CO) (%)	FE (H_2) (%)
3D-CTU-MCOF	-1.2	7.2	5.9	3.5	3.9	15.7	14.9	48.6
	-1.4	8.5	13.4	4.2	2.4	12.5	20.5	38.1
	-1.6	9.3	15.6	4.5	3.2	13.4	21.6	29.4
	-1.8	10.1	16.3	4.3	2.8	14.3	21.4	25.8
	-2.0	9.4	8.9	4.2	2.6	12.4	21.6	39.4
	-2.2	8.1	3.6	2.4	2.3	12.7	18.4	49.9
Cu_3L	-1.2	1.2	/	/	/	8.7	10.1	80.7
	-1.4	3.5	/	/	/	7.5	22.4	70.3
	-1.6	3.8	/	/	/	6.4	25.6	67.4
	-1.8	2.9	/	/	/	6.3	30.4	58.4
	-2.0	1.4	/	/	/	5.4	25.6	68.5
	-2.2	0.8	/	/	/	2.7	20.2	74.6

Section S2: FTIR spectra

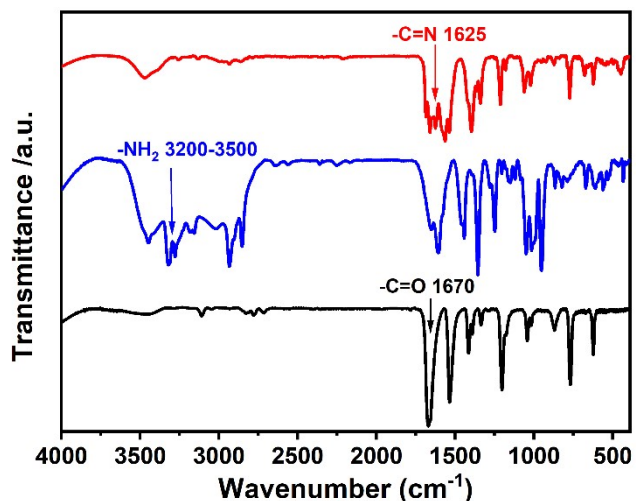


Fig. S1 FT-IR spectra of 3D-CTU-MCOF (red), TAA (blue), and Cu₃L(black).

Section S3: Solid-state ^{13}C NMR spectra

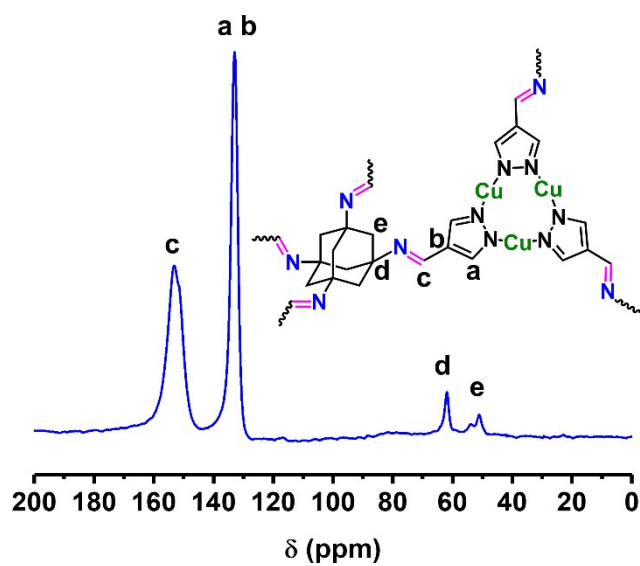


Fig. S2 Solid-state ^{13}C NMR spectrum of 3D-CTU-MCOF.

Section S4: TGA curves

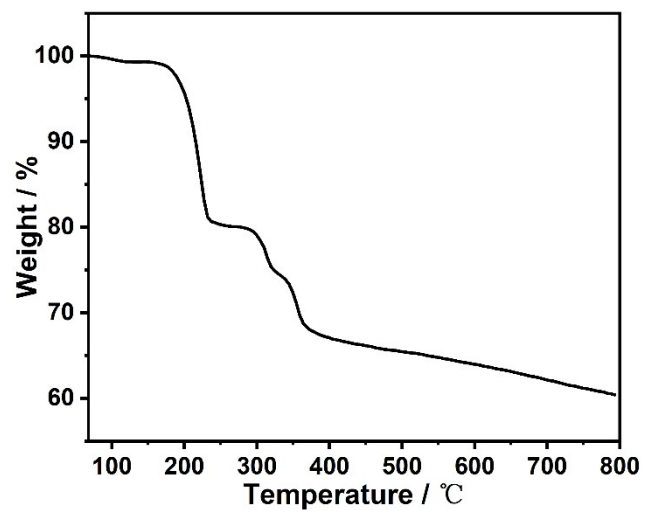


Fig. S3 TGA curve of 3D-CTU-MCOF.

Section S5: PXRD patterns and structures

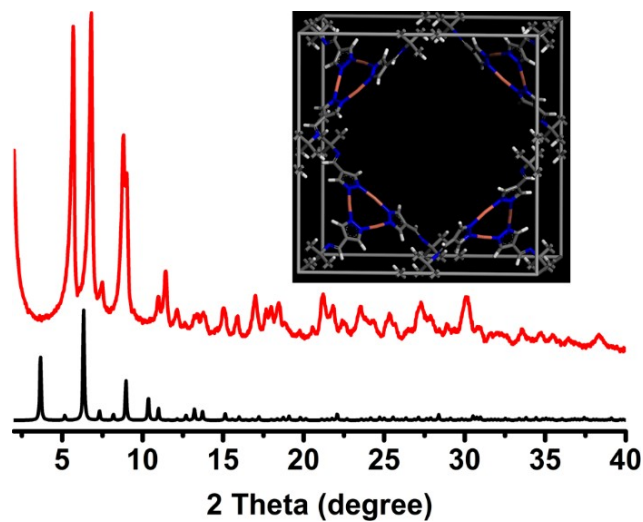


Fig. S4 PXRD patterns of 3D-CTU-MCOF: experimental (red) and simulated (black) with non-interpenetrated **bor** topology. Inset: its structural representation.

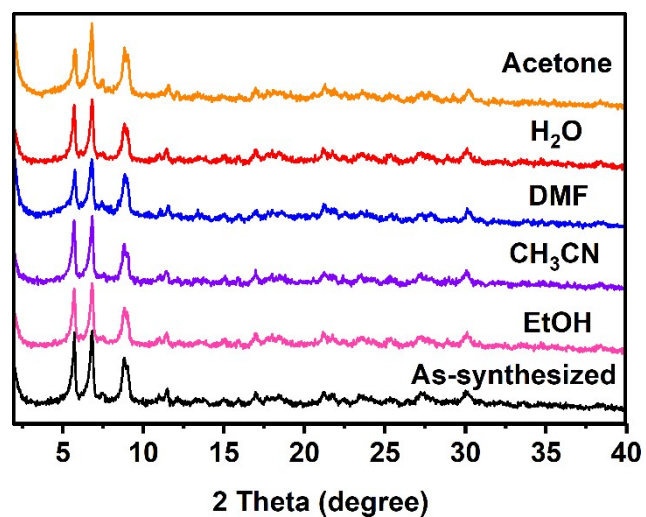


Fig. S5 PXRD patterns of 3D-CTU-MCOF in different solvents for 24 h.

Section S6: Nitrogen adsorption analysis

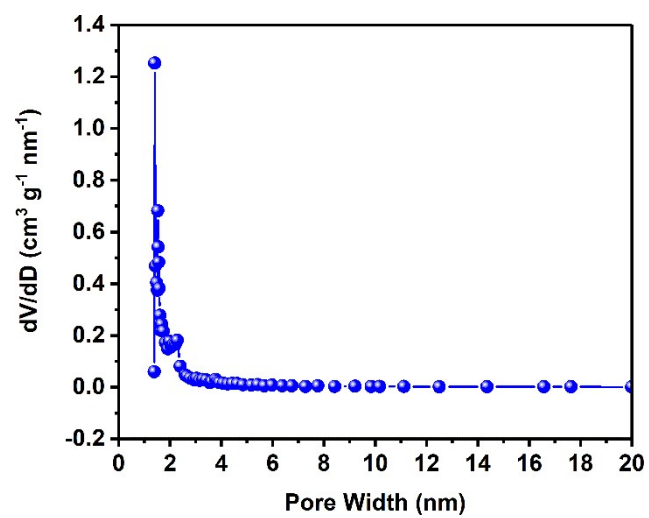


Fig. S6 Pore size distribution of 3D-CTU-MCOF obtained by NLDFT calculation.

Section S7: X-ray photoelectron spectroscopy (XPS)

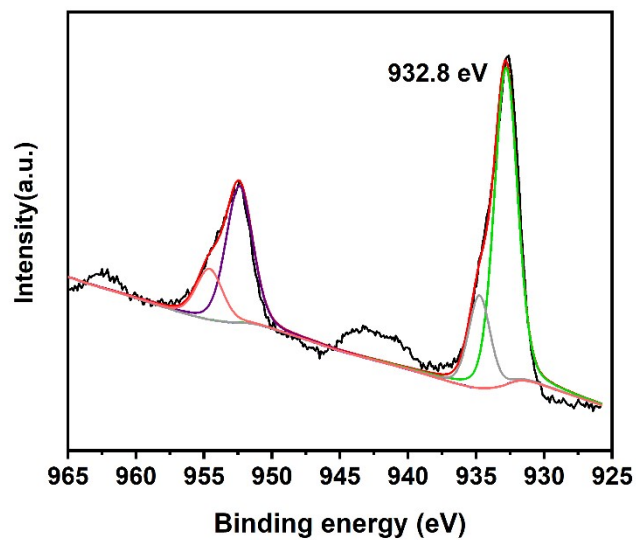


Fig. S7 XPS data of 3D-CTU-MCOF.

Section S8: Electrochemical measurements

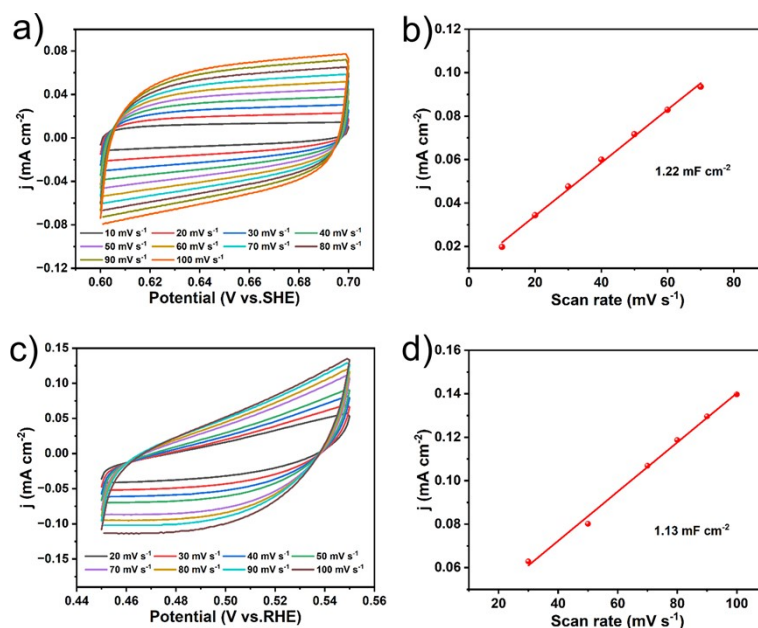


Fig. S8 Electrochemical double-layer capacitance (C_{dl}) measurements were used to determine the electrochemically accessible surface area (ECSA) of the material. Cyclic voltammograms of 3D-CTU-MCOF (a) and Cu_3L (c) at different sweep rates in the non-Faraday region; plots of the current density with different scan rates range for 3D-CTU-MCOF (b) and Cu_3L (d).

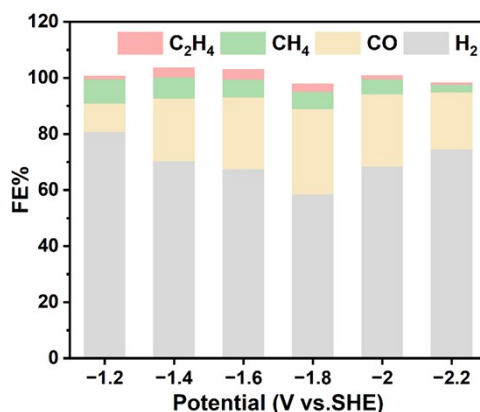


Fig. S9 Faradaic efficiency of different products with Cu_3L as a catalyst at different potentials.

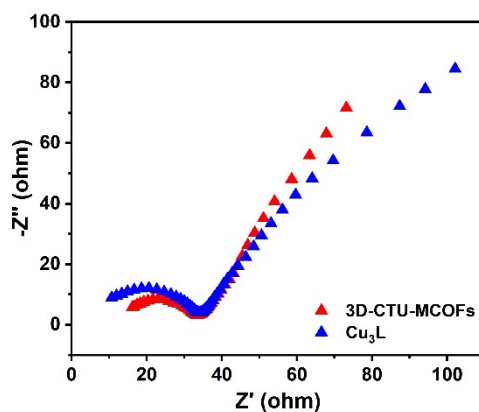


Fig. S10 Electrochemical impedance spectroscopy (EIS) of 3D-CTU-MCOF (red) and Cu_3L (blue) at open circuit potential

Section S9: Unit cell parameters and fractional atomic coordinates

Table S2. Unit cell parameters and fractional atomic coordinates for 3D-CTU-MCOF calculated based on the non-interpenetrated **ctn** net.

Space group	<i>I</i> -43d		
Calculated unit cell	$a = b = c = 37.2424 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$		
Measured unit cell	$a = b = c = 37.8218 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$		
Pawley refinement	$R_p = 3.59\%, wR_p = 5.76\%$		
atoms	x	y	z
N1	0.30219	0.73114	0.66391
N2	0.34952	0.77322	0.75375
C3	0.35644	0.81127	0.79704
C4	0.38390	0.78674	0.79977
C5	0.37875	0.76294	0.77195
N6	0.43595	0.76094	0.82681
C7	0.41265	0.78671	0.82638
C8	0.46662	0.75663	0.85101
Cu9	0.67216	0.75007	0.70884
C10	0.21033	0.62472	0.47346
C11	0.25	0.66212	0.5
H12	0.35166	0.83408	0.81415
H13	0.39515	0.74010	0.76522
H14	0.41367	0.80844	0.84537
H15	0.18611	0.64146	0.47769
H16	0.20547	0.60720	0.44992

Table S3. Unit cell parameters and fractional atomic coordinates for 3D-CTU-MCOF calculated based on the non-interpenetrated **bor** net.

Space group		<i>P23</i>	
Calculated unit cell		$a = b = c = 24.2732 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$	
atoms	x	y	z
N1	0.83504	0.70002	-0.84995
N2	0.87077	0.70748	-0.80953
C3	0.67305	0.8166	-0.91357
C4	0.64210	0.86337	-0.90391
C5	0.66003	0.88347	-0.85368
N6	0.57233	0.92967	-0.92673
C7	0.60497	0.89048	-0.943
C8	0.53726	0.96288	-0.96318
Cu9	1.23147	1.24887	1.13729
H10	0.67242	0.79107	-0.95011
H11	0.64776	0.92159	-0.83409
H12	-0.60677	0.87843	-0.98589
H13	0.52518	1.101	1.02696
H14	0.52599	0.97385	0.89969
H15	0.39909	0.97421	1.02639
C16	1	1	1.57371
C17	0.92609	1	1.5
C18	1	0.92697	1.5

Section S10: References

[S1] X. Li, J. Wang, F. Xue, Y. Wu, H. Xu, T. Yi,* and Q, Li.* *Angew. Chem. Int. Ed. Engl.*, 2021, 60, 2534-2540.