Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

Redox-Active Covalent Organic Nanosheet (CON) as Metal-free Electrocatalyst for Selective CO_2 Electro-Reduction to Liquid Fuel Methanol

Soumitra Barman[a], Anupam Dey[a], Faruk Ahamed Rahimi[a], Vasudeva Rao Bakuru[a], Rohan Jena[a], Adrija Ghosh[b], Tapas Kumar Maji[a,b]*

a. Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research Bangalore-560064, India.
b. New Chemistry Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Post, Bangalore 560064, India

E-mail: tmaji@jncasr.ac.in

Physical Measurement

Thermal stability was studied using the Mettler Toledo TGA 850 instrument in the temperature range of 30-800 °C with a heating rate of 5 °C/min in the N_2 atmosphere. Powder X-ray diffraction data was collected on a Bruker D8 discover instrument using Cu-Kα radiation. Field Emission Scanning Electron Microscope (FESEM) images were collected using Bruker Leica-S440I FESEM instrument. Samples for FESEM studies were prepared on a silicon wafer and a high vacuum with 100 kV accelerating voltage was applied during FESEM analysis. Energy dispersive spectroscopy (EDS) analysis was performed with an EDAX genesis instrument attached to the FESEM column. Transmission Electron Microscopic (TEM) images were captured using JEOL JEM-3010 TEM with an accelerating voltage of 300 kV. The COF material was taken in ethanol and drop-casted over a carbon-coated copper grid prior to TEM analysis. ^{1}H-NMR spectra were recorded at 600 MHz frequency using a JEOL Varian Inova 600 MHz spectrometer or 500 MHz Bruker spectrometer. ^{13}C-spectrum was recorded in the same NMR spectrometer at the frequency of 150 MHz.

Experimental Section:

Preparation of TPA-TPA COF

The TPA-TPA COF was synthesized following the methodology outlined in the previous report. In brief, a mixture containing TPA-3NH_2 (28.0 mg, 0.096 mmol), TPA-3CHO (31.7 mg, 0.095 mmol), and acetic acid (6 M, 0.5 mL) was combined in a glass ampoule with 1,4-dioxane/mesitylene (2 mL/2 mL). To ensure purity, the mixture underwent three freeze/pump/thaw cycles to remove any gases. Subsequently, the tube was sealed using a flame and heated to 120 °C for 96 hours.

After allowing the reaction to cool to room temperature, a yellow precipitate formed. This precipitate was thoroughly washed with THF, MeOH, and acetone, sequentially. The resulting material was then dried under vacuum at 120 °C overnight, resulting in the formation of a yellow solid with a yield of 85%.

The bulk crystal of TPA-TPA COF was transformed into nanosheets (CON) by high-frequency sonication for 2 h.

Electrochemical measurements

All electrochemical measurements were carried out at ambient temperature and pressure a CHI 760E potentiostat. A three-electrode cell configuration was employed with a working electrode of glassy carbon electrode of 3 mm diameter, a counter electrode of platinum plate (1 × 2 cm^2), and a reference electrode of Ag/AgCl (1M KCl). All potentials were calculated and presented with respect to the reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.197$ V, at 25°C), unless otherwise mentioned.

CV and LSV measurements

To prepare the catalyst ink, 1 mg of TPA-TPA-COF catalyst, 1 mg of carbon black and 25 µl of 5% Nafion 117 solution, as conducting binder, were introduced into 975 µl of water/isopropanol (12:1) solution and sonicated for 3 h. A glassy carbon electrode with diameter of 3 mm (Area: 0.07065 cm^2) was used for CV and LSV measurements. For comparison, CV measurements were also performed in an Ar (99.99%)-saturated electrolyte. The linear sweep voltammogram (LSVs) were collected at a scan rate of 10 mV s^{-1}.

Electrolysis in an H-type cell

Carbon fiber paper (CFP) (Global Nanotech, thickness ~ 270 μm) was used as received and cut into 1 cm × 1 cm^2 as the working electrode while performing controlled potential electrolysis in a custom-made H-type cell (Fig. S6).

The two compartments was separated using Nafion 117 membrane. The cathodic compartment was comprised of CFP as working electrode and Ag/AgCl as reference electrode whereas Pt plate was used as counter electrode in anodic compartment. An aliquot of 50 μL of the catalyst ink was drop-casted onto a CFP (0.5 x 1 cm^2) and allowed to dry in air overnight, giving a catalyst loading of 0.05 mg cm^{-2}.

0.2 M phosphate buffer electrolyte was used for both chambers. The volume of the working electrode chamber is 65.0 mL. 40.0 mL of electrolyte was added into this chamber. The volume of the head-space in the working-electrode chamber is 35.0 mL. A CO_2-saturated electrolyte was prepared by purging CO_2 (99.99%) into aqueous solution of phosphate buffer for 30 min, and a flow of 30 sccm CO_2 was maintained over the electrolyte throughout the electrochemical measurements. At first, 20 cycles of CV sweep between -0.27 V and -0.67 V vs. RHE were conducted to generate stable CV curves. Chronoamperometry was performed for 2 h at each potential for CO_2 reduction tests in the H-type cell.

Electrolysis was carried out in 0.2 M phosphate buffer of pH 7.2, if not mentioned otherwise.

The Tafel slope was calculated based on the Tafel equation ($\eta = b \log(j_{CH3OH}/j_o)$), where η is the overpotential, b is the Tafel slope, j_{CH3OH} is the current density for CH_3OH formation, and j_o is the exchange current density. All current densities were normalized to the geometrical area of electrode. Roughness factor (RF) was calculated as the ratio of the electrochemically active surface area (ECSA) on the electrode to the geometric area of the disk electrode. Based on the definition: ECSA = C_{dl}/C_s (double layer capacitance/specific capacitance), C_{dl} corresponds to the slope of the double-layer charging current versus the scan rate (ν) plot; we used a specific capacitance (Cs) value for blank CFP.

Each geometric current density (j_{tot}) at a given potential was the 2-hour averaged current density of the chronoamperometry curve.

The partial current density of the products was calculated according to:

$$j_{partial} = j_{tot} \cdot FE_{product}$$

Calculation of overpotential:

The overpotential η is the difference between the actual electrode reduction potential and the thermodynamic potential, defined by the following equation:[1]

Overpotential (η) = $E_{applied}$ (RHE) – $E^{0}_{CO_2/MeOH}$ (RHE)

In the equation, $E_{applied}$ is the applied potential (vs. RHE) and $E^{0}_{CO_2/MeOH}$ is the standard reduction potential for CO_2 to methanol conversion which is 0.03 V (vs. RHE).

EIS was carried out at 100 mV alternating current voltage amplitude in a frequency range from 0.01 Hz to 100 kHz under a biased voltage of -0.78 V (vs. RHE). The set-up was the same as that of the CV and chronopotentiometry and the EIS was performed in a CO_2-saturated 0.2 M phosphate buffer solution.

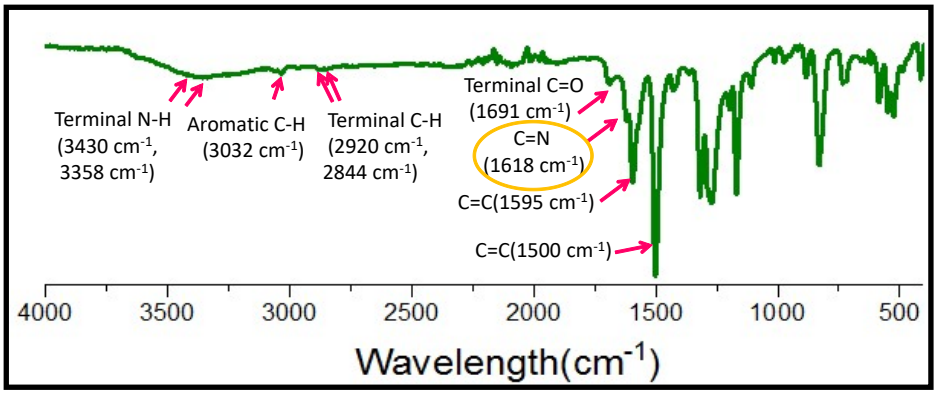


Fig. S1. FT-IR spectra of TPA-COF showing the characteristic peaks.

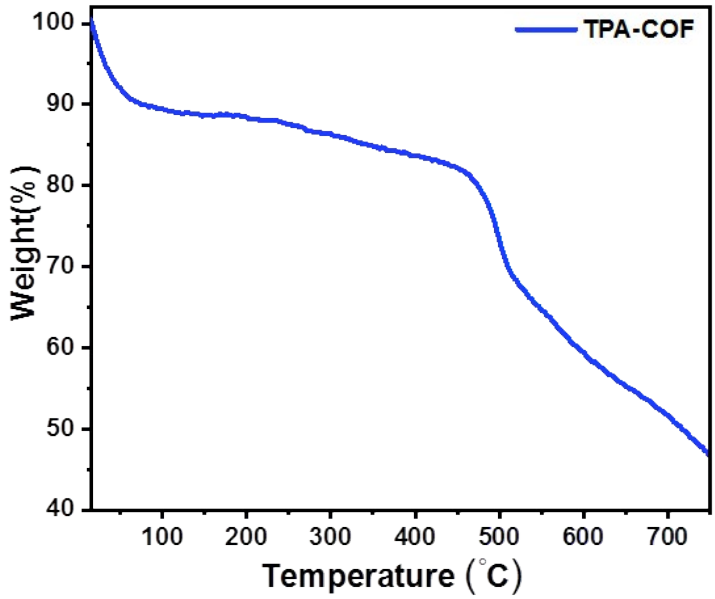


Fig. S2. Thermogravimetric profile of TPA-TPA-COF under the N_2 atmosphere.

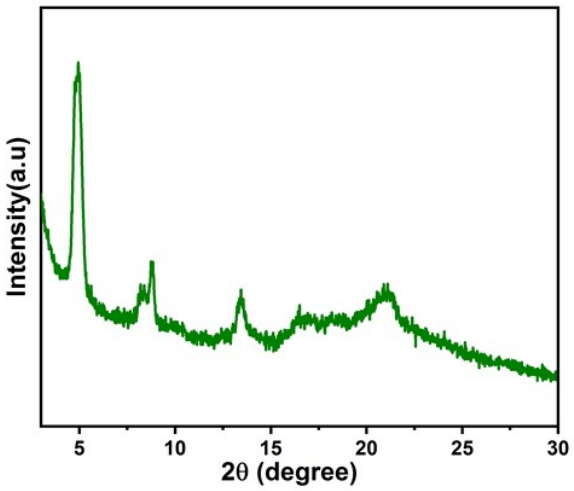


Fig. S3. PXRD-Pattern of TPA-TPA-COF nanosheet (CON).

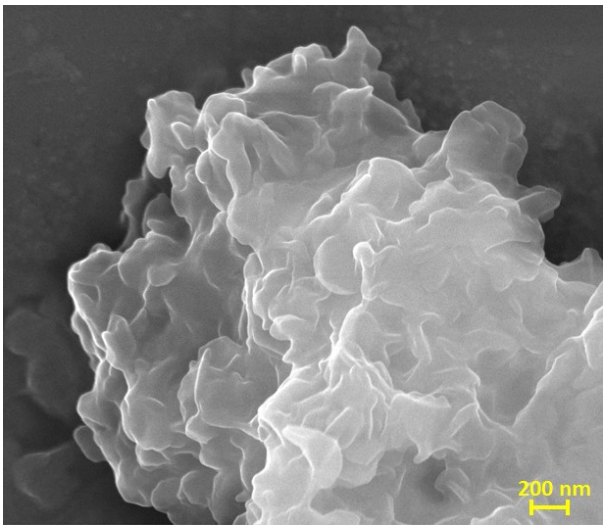


Fig. S4. SEM image of TPA-TPA-COF.

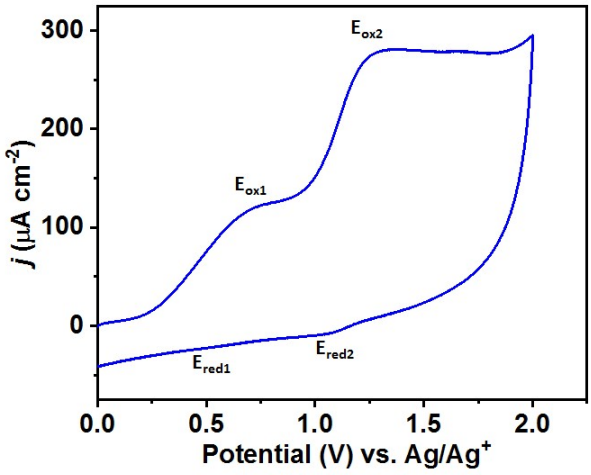


Fig. S5. Cyclic voltammetry (CV) diagram of TPA-TPA-COF in acetonitrile medium using tetrabutylammonium hexafluorophosphate (TBAHFP) as electrolyte.

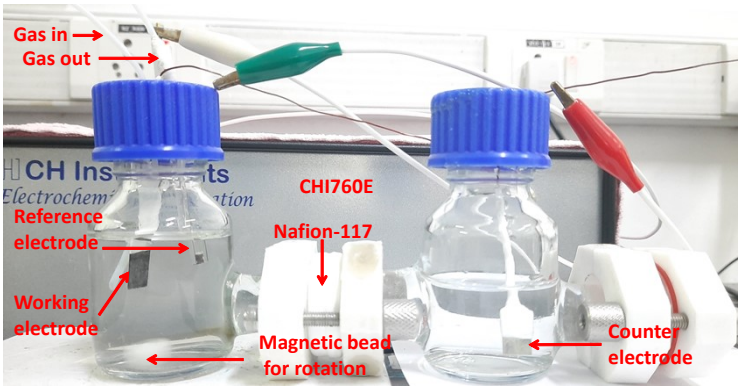


Fig. S6. Photograph of the used H-type cell during electrochemical CO_2RR.

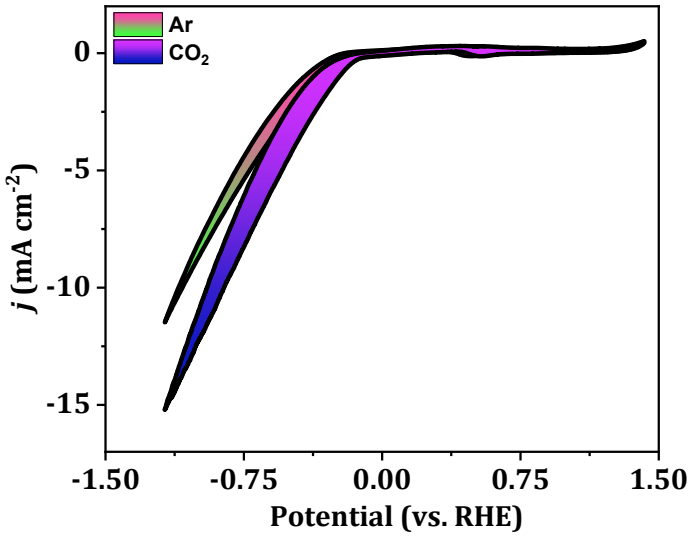


Fig. S7. Cyclic voltammogram plots showing the activity in Argon (Ar) and CO_2 saturated phosphate buffer.

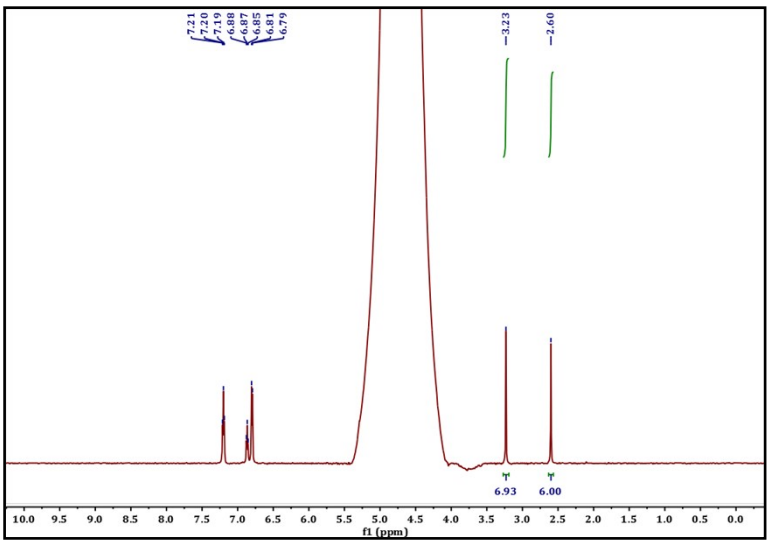


Fig. S8. [1]H-NMR spectrum after electroreduction at -0.78 V for 2 h. Water suppression method was utilized to suppress water peak. 4 mM DMSO and 20 mM phenol was used as external standard to find the concentration of the liquid products. Methanol was integrated against DMSO for the calculation.

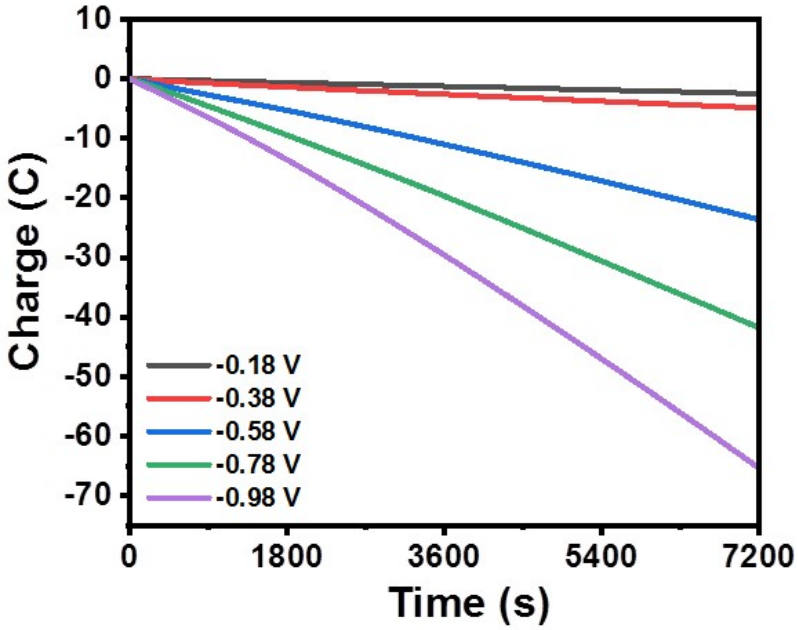


Fig. S9. Plot showing the total charge passed during 2 h of electroreduction.

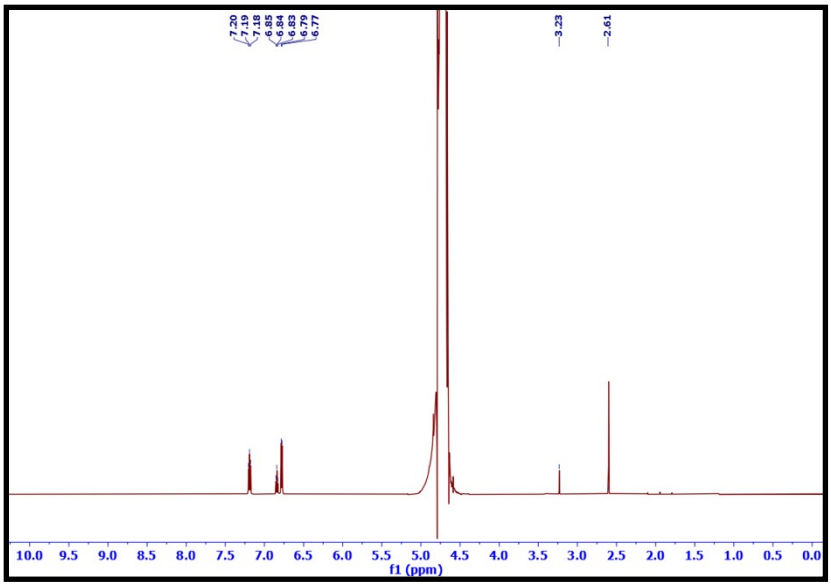


Fig. S10. ^{1}H-NMR spectrum over TPA-TPA-COF electrode at an overpotential of 210 mV in 0.2 M phosphate buffer (pH-7.2).

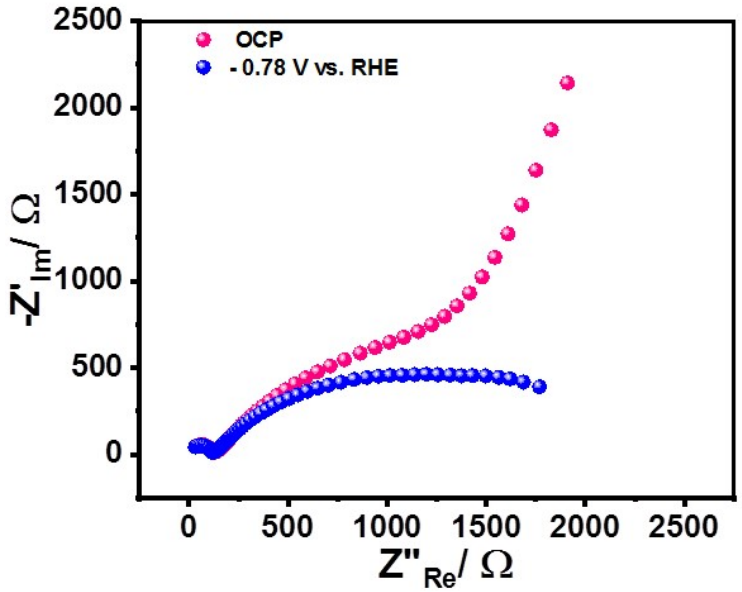


Fig. S11. Nyquist plot at open circuit potential (OCP) and at -0.78 V vs. RHE showing charge transfer resistance.

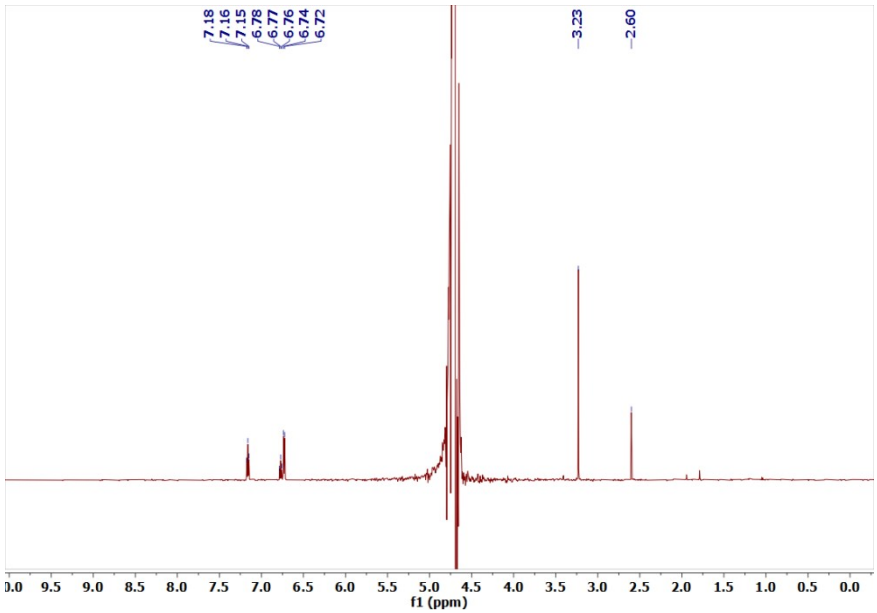


Fig. S12. [1]H-NMR spectrum over TPA-TPA-CON electrode at -0.78 V in 0.2 M phosphate buffer after long-term electrolysis for 12 h (pH-7.2).

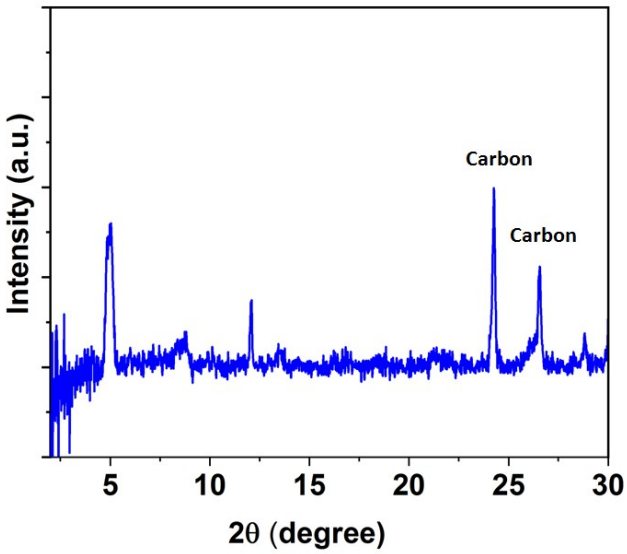


Fig. S13. PXRD pattern of TPA-TPA-COF after electrolysis at -0.78 V vs. RHE.

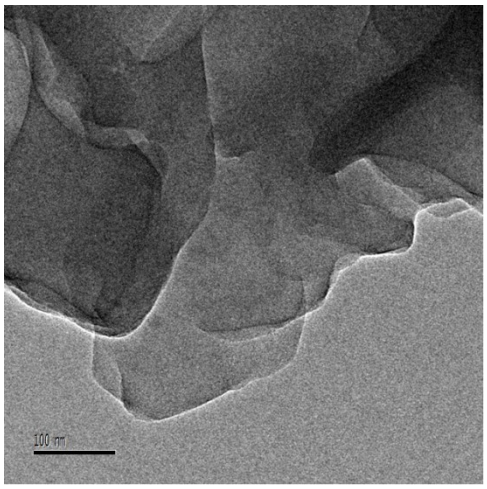


Fig. S14. HRTEM image of TPA-TPA COF after electrolysis at -0.78 V vs. RHE.

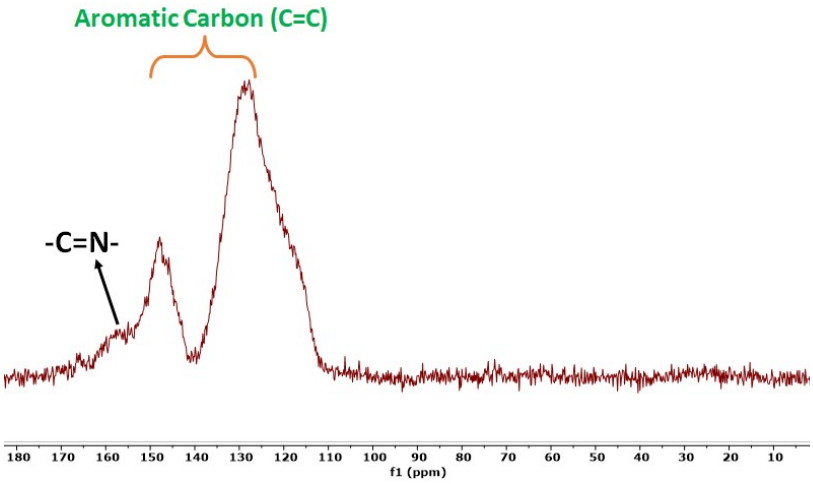


Fig. S15. Solid state ^{13}C-NMR spectra of TPA-TPA COF after electrolysis at -0.78 V vs. RHE.

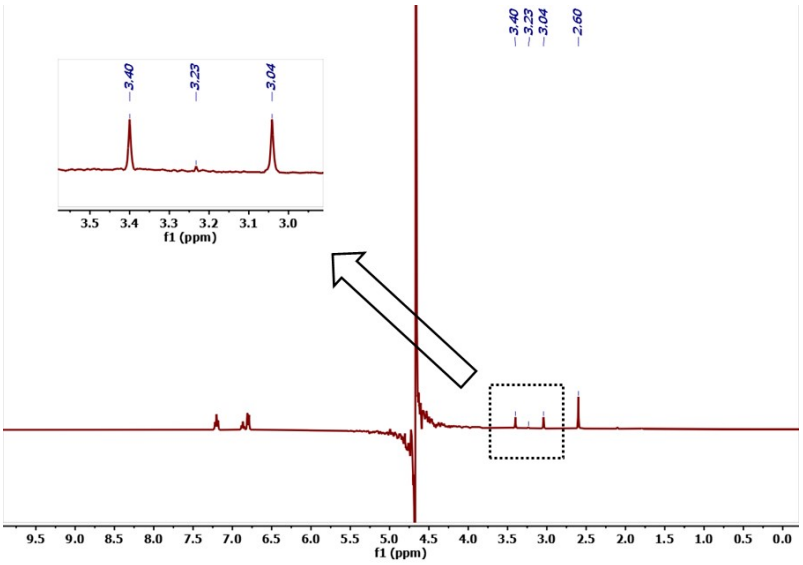


Fig. S16. ^{1}H-NMR spectrum over TPA-TPA-COF electrode using $^{13}CO_2$ as feeding gas. The splitting of the singlet peak of methanol demonstrates the production of $^{13}CH_3OH$.

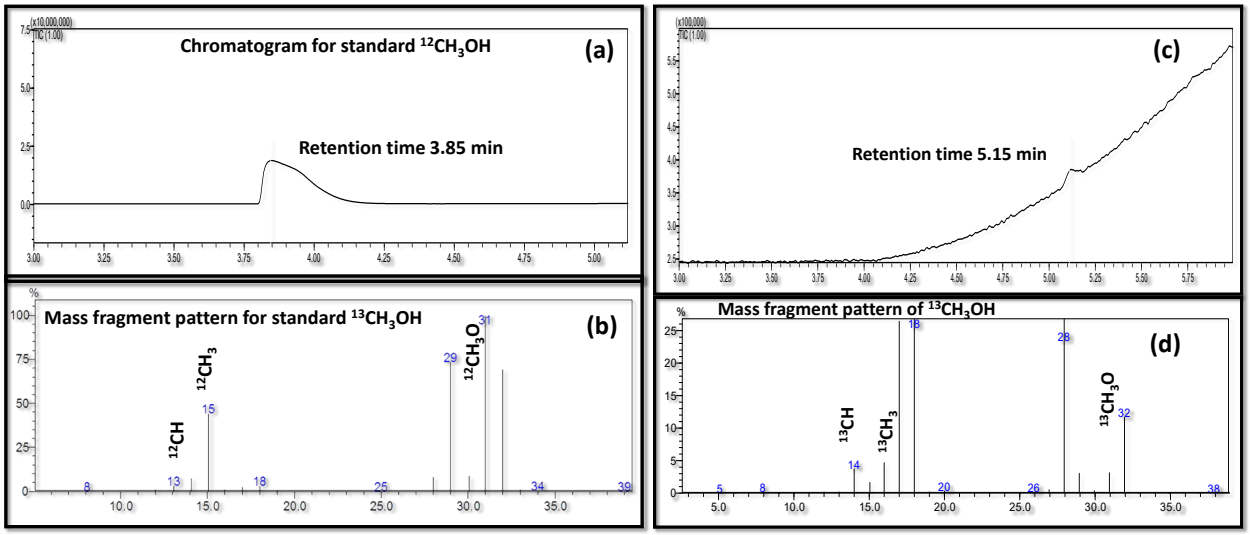


Fig. S17. (a) Chromatogram for standard methanol (b) Mass spectrum obtained from GC-MS using standard methanol (c) Chromatogram for methanol detection using $^{13}CO_2$ as feeding gas for electro reduction over TPA-TPA-COF (d) Mass spectra for $^{13}CH_3OH$ obtained from GC-MS.

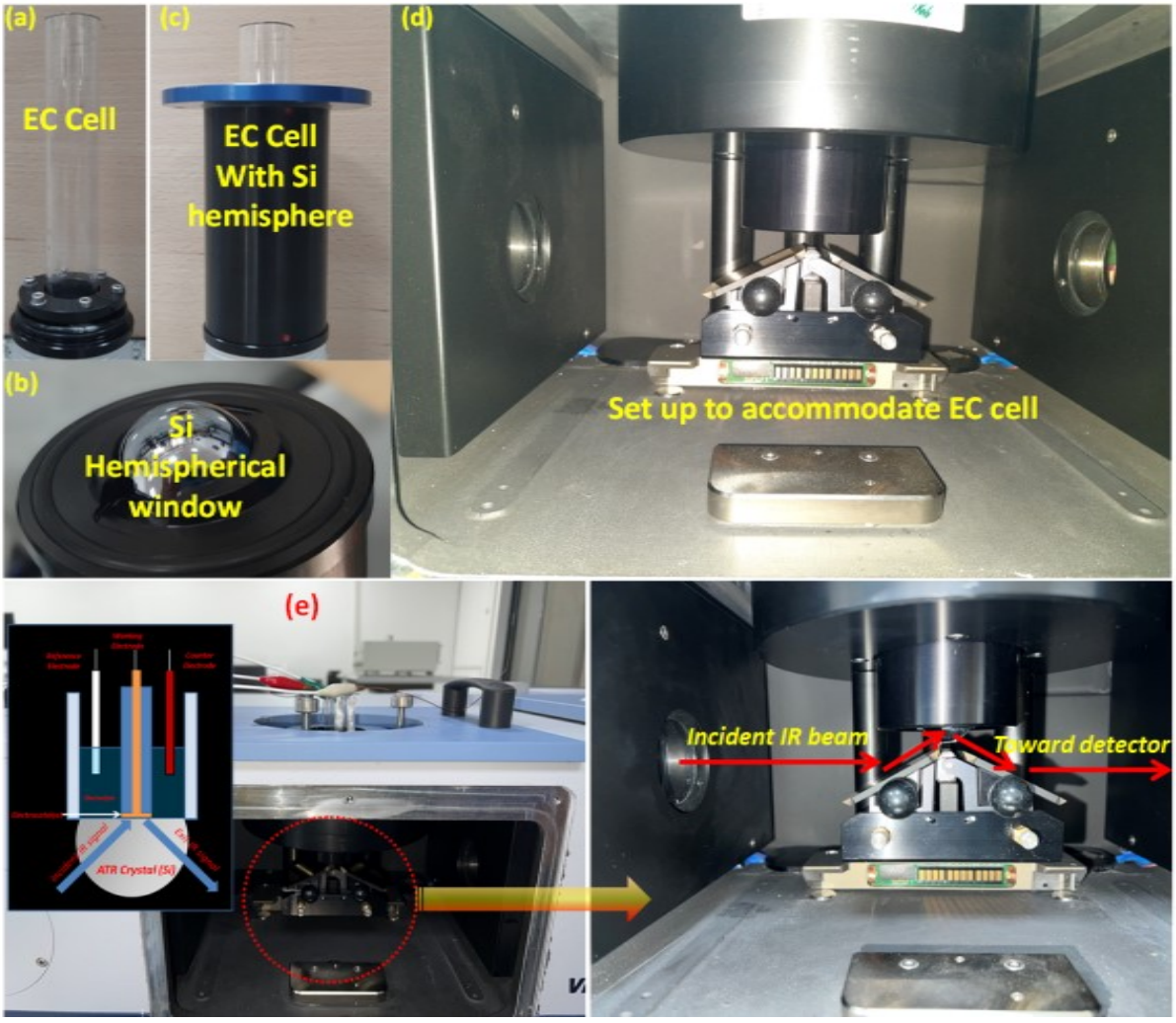


Fig. S18 (a) Electrochemical cell (EC) used for in-situ IR measurement (b) Picture of Si-hemisphere used during in-situ measurement (c) Photograph of EC cell connected with Si hemisphere (d) Attachments used during in-situ measurement. (e) Photograph of the overall set up, including the schematic of the measurement process.

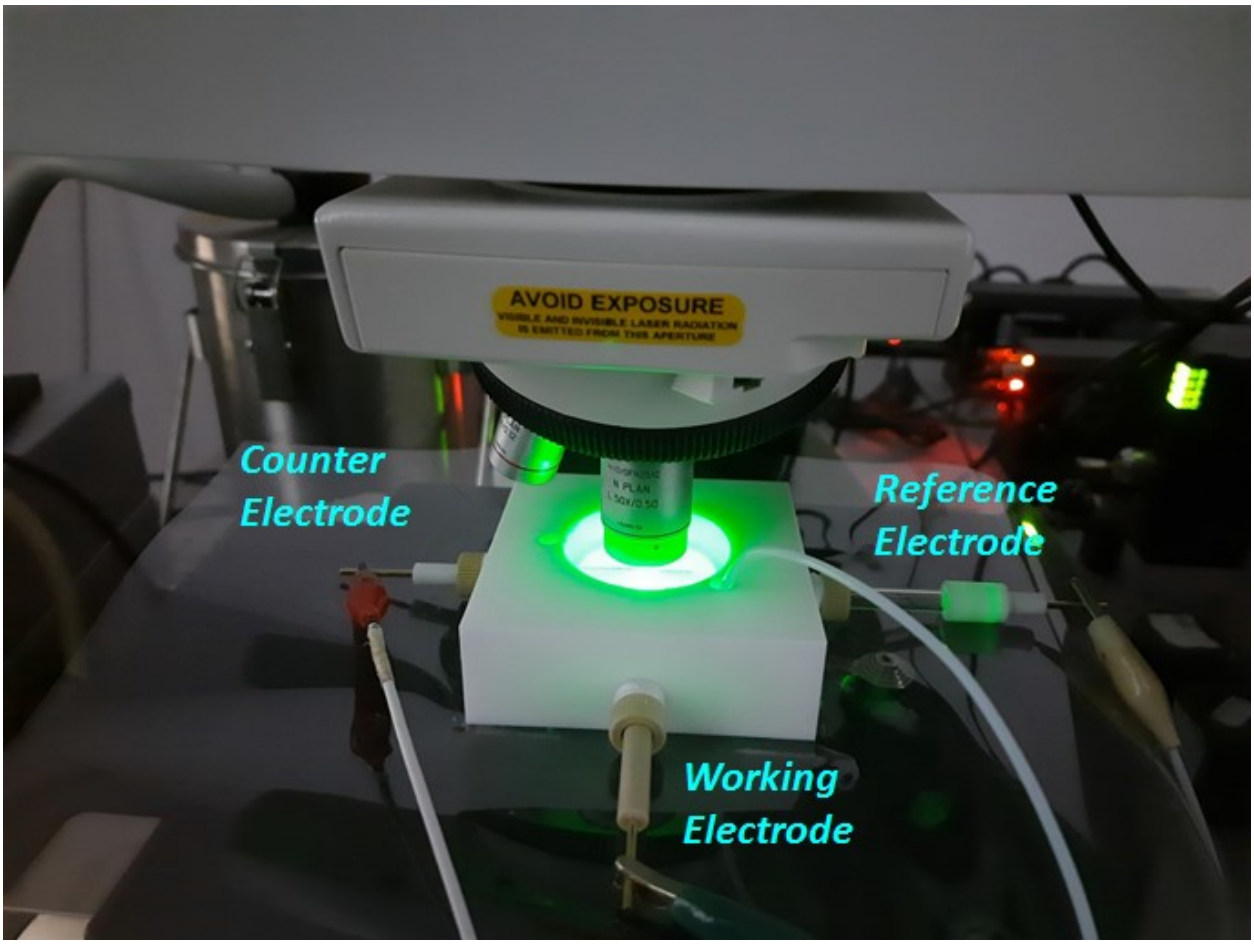


Fig. S19 Photograph of *in situ* Raman set up during electrochemical CO_2 reduction

Calculation of Faradaic efficiency for liquid product

The Faradaic efficiency of liquid product was calculated using the following equation:[2]

$$FE = \frac{z.n.F}{Q}$$

Where, z= the number of electron exchanged (here in case of CO_2 reduction to methanol, z=6)

N= Number of moles of product

F= Faraday's constant (F=96485 C/mol)

Q= Total charge passed (C)

From Fig. S8, the ratio of [DMSO] and [MeOH] was obtained using integration value.

[DMSO]/[MeOH] = [6/6]/[6.93/3] = 0.4329

[MeOH] = [DMSO]/0.4329 ----------(1)

Now, during NMR sample preparation 400 µl aliquot was taken along with 50 µl D_2O and 50 µl external standard.

So effective strength of DMSO in the NMR tube is 0.4 mM;

From equation 1, we found [MeOH] = 0.924 mM

The amount of MeOH in 0.4 ml = 0.3696 µmol

In a total of 40 ml solution, the amount of MeOH = 36.96 µmol

From Fig. S9, we found the total amount of charge passed during 2 h to be 41.5 C.

$$\text{So, FE\%} = \frac{36.96 \times 10^{-6}\, mol \times 6 \times 96485\, C\, mol^{-1}}{41.5\, C} \times 100\% = \mathbf{51.56}\ \%$$

Calculation of Faradaic efficiency for gaseous products

Faradaic efficiencies for the formation of gas products were calculated as follows:[2]

$$\text{FE\%} = \frac{n.F.V.v.P^0}{R.T.i} \times 100\%$$

Where, n is the number of electrons required for products (for CO formation it is 2), V (vol %) is the volume concentration of gas in the gasbag from electrochemical cell, ν (ml min^{-1} at room temperature and ambient pressure) is the gas flow rate, i (mA) is the steady-state cell current, P = 1.01 x 10^5 Pa, T = 273.15 K, F = 96485 C mol^{-1}, and R = 8.314 J mol^{-1} K^{-1}.

For example, the amount of CO obtained from GC after 2 h of electroreduction = 82.16 ppm. The flow rate was 30 ml $min^{-1,}$ which was controlled throughout the experiment using HORIBA S600 Mass Flow Device.

$$\text{So, FE\%} = \frac{2 \times 96485\, C\, mol^{-1} \times 82.16 \times 10^{-6} \times (\frac{30}{60\, sec} \times 10^{-6} m^3) \times 1.01 \times 10^5 Pa}{8.314\, J\, K^{-1} mol^{-1} \times 273.15\, K \times 5.76 \times 10^{-3} C\, S^{-1}} \times 100\% = \mathbf{5.49\ \%}$$

Computational Details:

All the calculations were performed within the framework of density functional theory (DFT) model in Gaussian16 program package.[3] The geometry optimization and frequency calculations were performed utilizing B3LYP exchange-correlation functional along with 6-31+G** basis set for all atoms.[4-8] The calculations were performed in absence of any solvent. Grimme's d3 dispersion was also used to tackle weak interactions.[5] The harmonic vibrational frequency analysis of the optimized geometries was performed to confirm the nature of stationary points. All the optimized intermediates revealed the absence of any imaginary vibrational mode, indicating the optimized geometries as minima on the potential energy surface (PES). All thermochemical data were obtained with the ideal gas-rigid rotor-simple harmonic oscillator approximations at 298.15 K and 1 atm. Zero point-energy corrections were included in the Gibbs free energy values along with entropy effect and enthalpy effect. The pictures of the optimized structures were taken from Gauss View 6.0.16.

The electrocatalytic mechanisms were investigated based on Nørskov's computational hydrogen electrode (CHE) model. This model is frequently employed in theoretical investigations of electrocatalysis because it provides a useful way to examine proton-electron transport in electrocatalysis without explicitly treating solvated protons.[9-12] In CHE model, the energy of an $[e^- + H^+]$ pair is considered to be equal to half of the gaseous hydrogen (1/2 H_2) at an equilibrium potential:[13, 14]

$$G(e^- + H^+) = 1/2\ G(H_2) - neU$$

where n is the number of electrons involved in the reaction (n = 1), e is the electronic charge, and U is the external potential. For CO_2RR, the corrections of zero-point energy (E_{ZPE}), heat capacity (C_p), temperature (T) and entropy (S) are introduced into the DFT-calculated total energy (E_{total}) to determine the Gibbs free energy (G) of each intermediate species at 298.15 K:[14, 15]

$$G = E_{total} + E_{ZPE} + \int C_p dT - TS$$

The Gibbs free energies (G) for all the intermediate species were calculated by using E_{total} along with the aforementioned corrections and listed in Table S34. Hence, the Gibbs free reaction energy for each elementary step at 298.15 K should be:[16]

$$\Delta G = \Delta E_{total} + \Delta E_{ZPE} + \int C_p dT - T\Delta S$$

where ΔE_{total} is the difference of total electronic energy derived from DFT, ΔE_{ZPE} is the difference of zero-point energy correction (ZPE), $\int C_p dT$ is the enthalpy correction and $T\Delta S$ is the entropy change, as shown in Table S34. The Gibbs free energy change (ΔG) for each elementary step was calculated as:

$$\Delta G = \sum G(\text{Product}) - \sum G(\text{Reactant})$$

For the elementary steps involving proton-coupled reduction:[16]

$$\Delta G\,(U) = \sum G\,(U = 0) + neU$$

where n is the number of electrons involved in the reaction, e is the electronic charge and U is the applied external potential.

The pathways adopted for electrocatalytic CO_2 reduction to CH_3OH in this work are listed below:

$$* + CO_2 + H^+ + e^- \rightarrow *COOH$$

$$*COOH + H^+ + e^- \rightarrow *CO + H_2O$$

$$*CO + H^+ + e^- \rightarrow *CHO$$

$$*CHO + H^+ + e^- \rightarrow *OCH_2$$

$$*OCH_2 + H^+ + e^- \rightarrow *OCH_3$$

$$*OCH_3 + H^+ + e^- \rightarrow * + CH_3OH$$

In Fig. S19, the most suitable active center for COOH-binding (*COOH) was identified through DFT calculations of four *COOH intermediate models (model-**a** to model-**d**) by attaching -COOH on one of the four probable active centers (**a-d**). However, DFT calculations revealed that -COOH could not be bound to the active center in model-**a** and model-**d**, both of which have triphenyl amine (TPA) nitrogen as the active center. This left us with only two potential COOH-binding centers, imine nitrogen (**b**) and imine carbon (**c**). Gibbs free energy calculations showed that the formation of COOH-bound intermediate *COOH, where imine nitrogen is the active center, is the less uphill process (ΔG = +0.86 eV). This suggested that the imine nitrogen is the most suitable active center for COOH-binding during the CO_2RR on TPA-TPA COF.

In Fig. S20, all the intermediates involved in possible pathways for CO_2 electroreduction to CH_3OH on TPA-TPA COF catalyst were summarized.

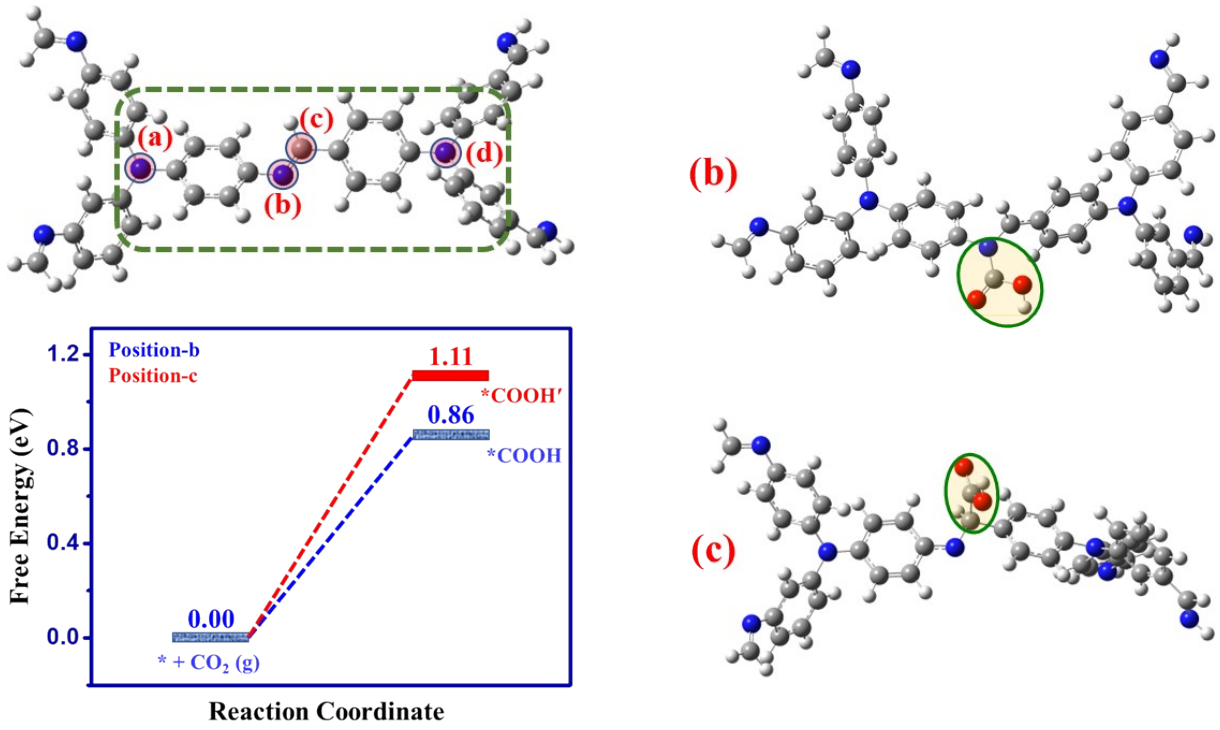
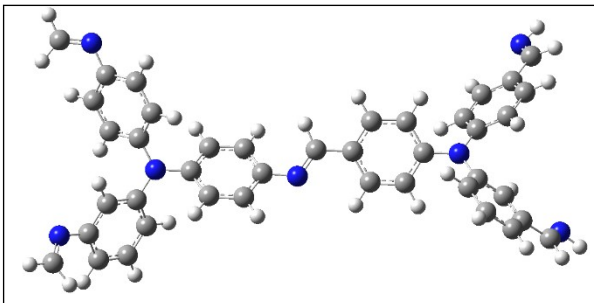
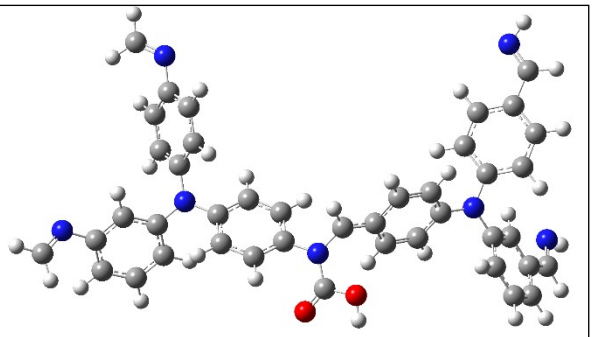


Fig. S20. Identification of the most suitable active center for COOH-binding (*COOH) during CO_2RR: Calculations with different COOH-bound models (model-**a** to model-**d**) by attaching -COOH on four probable active centers (**a-d**).



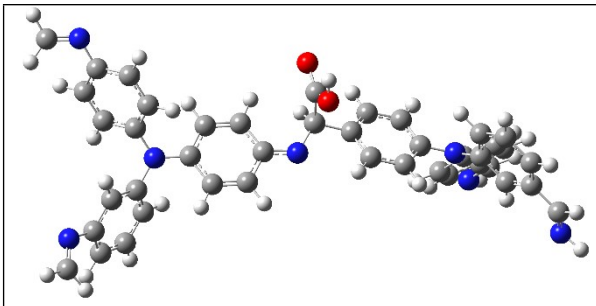
(1) TPA-TPA

(*)



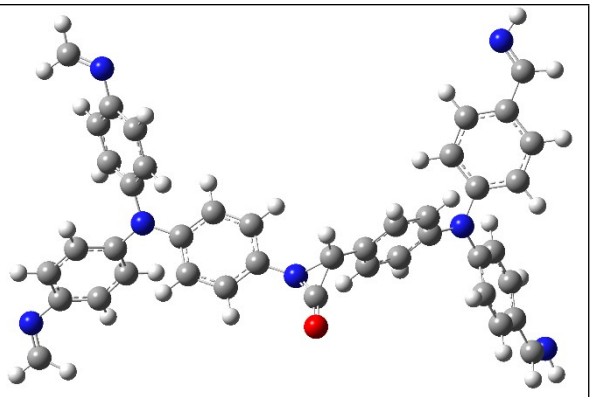
(2) TPA-TPA-COOH

(*COOH) (model-b)



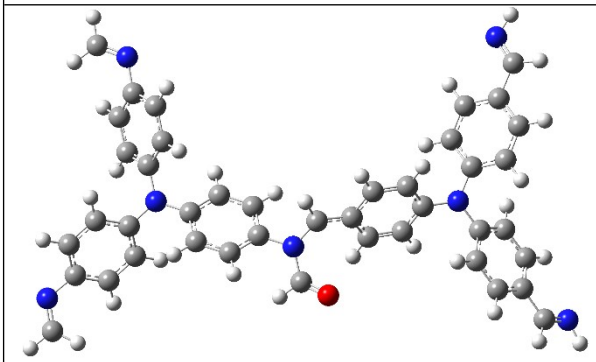
(2′) model-c

(*COOH′)



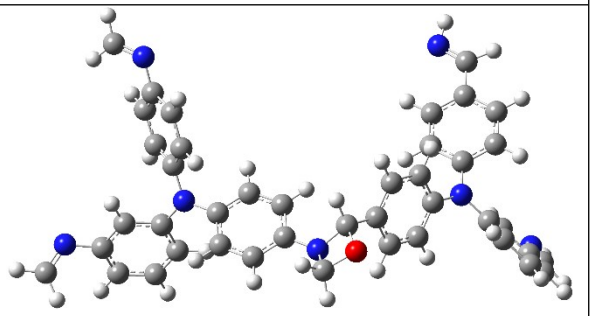
(3) TPA-TPA-CO

(*CO)



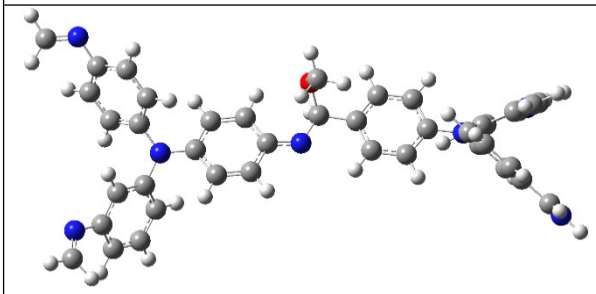
(4) TPA-TPA-CHO

(*CHO)



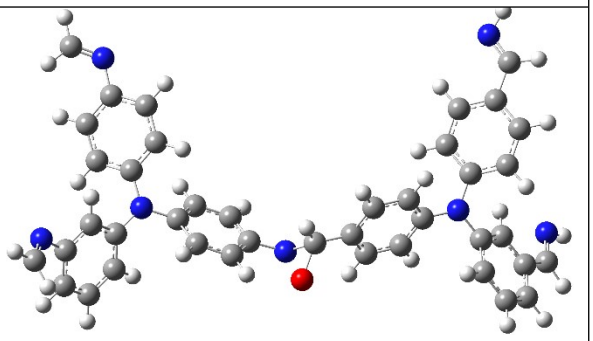
(5) TPA-TPA-OCH_2

(*OCH_2)



(6) TPA-TPA-OCH_3

(*OCH_3)



(7) TPA-TPA-O

(*O)

Fig. S21. Optimized geometries of all the intermediates.

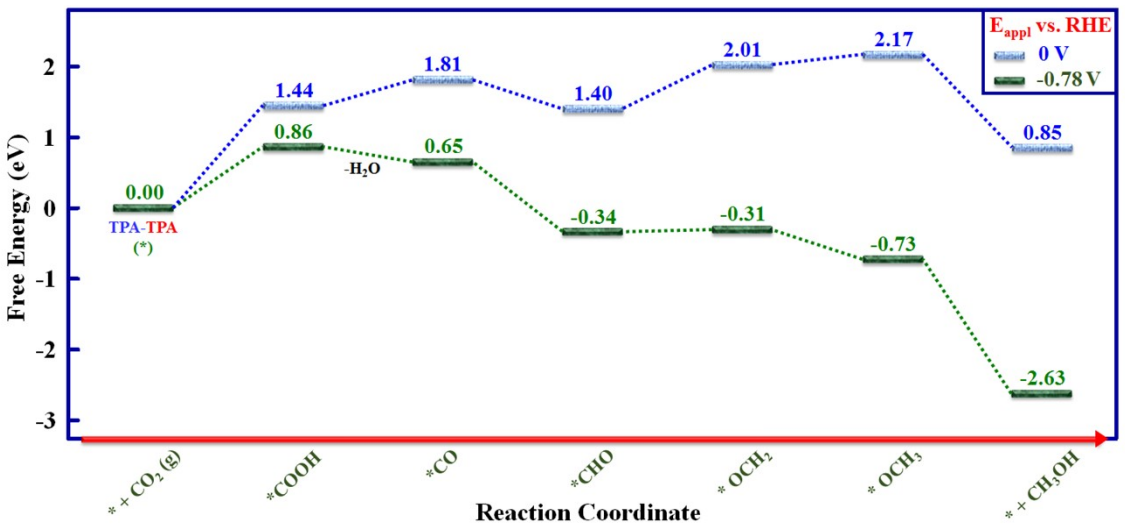


Fig. S22. Relative Gibbs free energy (ΔG) diagram computed by DFT, at an applied potential of 0 V (blue) and -0.78 V (green) vs. RHE for CO_2 to CH_3OH reduction process occurring on TPA-TPA COF. Asterisk (*) denotes the active site of TPA-TPA catalyst which is introduced to show the adsorbed intermediate species.

Table 1. Electrochemical reduction of CO_2 to CH_3OH using various state-of-art electrocatalysts.

Electrode/ electrocatalysts	**Electrode Potential (V)**	**Electrolyte**	**FE $_{methanol}$ (%)**	**References**
Mo-Bi BMC Nanosheet	-0.7 V vs. SHE	0.5 M [Bmim]BF_4 in CH_3CN	71.2	*Angew. Chem. Int. Ed.*,**2016**, 55, 6771
Cu $_{1.63}$ Se(1/3)	-2.1 V vs. Ag/Ag^+	[Bmim]PF_6 (30 wt.%)/CH_3CN/H_2O (5 wt.%)	77.6±2.0	*Nat. Commun.*, **2019**, 10**,** 677
FeP NA/TM	-0.20 V vs. RHE	0.5 M $NaHCO_3$	80.2	*Angew. Chem. Int. Ed.*, **2020**, 59, 758
$Fe_2P_2S_6$ Nanosheet	-0.20 V vs. RHE	0.5 M $NaHCO_3$	65.2	*ACS Catal.*, **2019**, *9*, 9721
Pd/SnO_2	-0.24 V vs.	0.1 M $NaHCO_3$	54.8±2	*Angew. Chem. Int. Ed.*, **2018**,

	RHE			*57*, 9475
Co/SL-NG	-0.90 V vs. SCE	0.1 M $NaHCO_3$	71.4	*ACS Appl. Mater. Interfaces* **2018**, *10*, 44403
$Co(CO_3)_{0.5}OH{\cdot}0.11H_2O$	-0.98 V vs. SCE	0.1 M $NaHCO_3$	97.0	*Green Chem.* ***2018****, 20, 2967*
PD-Zn/Ag foam	-1.38 V vs. RHE	0.1 M $KHCO_3$	10.5	*Angew. Chem. Int. Ed.* ***2019****, 58, 2256*
CuSAs/TCNFs	-0.9 V vs. RHE	0.1 M $KHCO_3$	44	*J. Am. Chem. Soc.,* ***2019,*** *141,12717*
TAPA-TFPA-COF (Metal-free)	-0.58 V vs. RHE	0.2 M Phosphate buffer	52.5	*This work*

Cartesian coordinates of the computed structures

Coordinates are given in standard XYZ format

Table S1. DFT-optimized geometry of **(1) TPA-TPA** (singlet) **(*)**, computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	-6.05613300	-0.13985900	-0.36124700
C	-6.66556200	-1.34765300	-0.80379300
C	-7.75163800	-1.88553800	-0.10857100
C	-6.17765500	-2.00586500	-1.94797000
C	-8.35991300	-3.06912400	-0.55154700
H	-8.13905200	-1.39330300	0.77657200
C	-6.76925500	-3.19199400	-2.37701300
H	-5.33621300	-1.58365800	-2.48730100
C	-7.86093200	-3.72509700	-1.68699700
H	-6.38516200	-3.69382900	-3.25999800
C	-4.64492600	-0.03730700	-0.33294500
C	-4.00414200	1.15615900	-0.70635400
C	-3.85897100	-1.13715200	0.06797400
C	-2.61614400	1.24396600	-0.67196400
H	-4.59802100	2.00762500	-1.02036300
C	-2.47533100	-1.04515200	0.08804200
H	-4.34781100	-2.05841500	0.36678100
C	-1.82549800	0.14920300	-0.28134600
H	-2.13589300	2.17384600	-0.96721000
H	-1.87197800	-1.88969900	0.40403100
C	-6.86760400	0.95241700	0.03496100

C	-8.04973900	1.25164100	-0.66073600
C	-6.50410100	1.74752300	1.14016800
C	-8.84674200	2.31846500	-0.25469400
H	-8.34012400	0.64489300	-1.51147300
C	-7.29734300	2.81709900	1.52921100
H	-5.59844300	1.51232800	1.68910000
C	-8.48494500	3.12136000	0.83793600
H	-9.75962100	2.53756100	-0.80364500
H	-7.02186100	3.42537800	2.38439800
H	-8.32592700	-4.64621700	-2.02846400
C	-0.36849700	0.27507200	-0.26621800
H	0.02601600	1.26256200	-0.55093100
N	0.41225100	-0.69894200	0.03653200
C	1.79933100	-0.50347500	0.10355200
C	2.63414900	-1.57091000	-0.27391900
C	2.40308400	0.67925600	0.57593300
C	4.01832500	-1.44364800	-0.24266200
H	2.17343100	-2.49096900	-0.61944800
C	3.78817000	0.79522800	0.64136700
H	1.78355000	1.49327900	0.94023200
C	4.61525200	-0.25826900	0.21885500
H	4.64815900	-2.26727600	-0.56255500
H	4.24004000	1.70348000	1.02699400
N	6.02867700	-0.13114400	0.27369700
C	6.64232800	1.07792600	-0.14289600
C	6.81957600	-1.20607200	0.75277500
C	7.70985200	1.62760500	0.58684100
C	6.17593900	1.76225000	-1.27857000
C	8.05139600	-1.50104500	0.15270300
C	6.38290200	-1.97880700	1.84419400
C	8.31630000	2.80962600	0.17302000
H	8.05852100	1.12332900	1.48204400
C	6.75796600	2.96405700	-1.66726200
H	5.34490600	1.35268300	-1.84298100
C	8.83031400	-2.56860300	0.61461100
H	8.41265200	-0.90962900	-0.68099300
C	7.17012200	-3.03012300	2.31030700
H	5.43942400	-1.74284400	2.32389900
C	7.85717900	3.49022800	-0.96947600
H	9.12135900	3.23264800	0.76653600
H	6.38781300	3.49968800	-2.53567200
C	8.39325300	-3.33497900	1.70891100
H	6.83424100	-3.60677500	3.16741900
H	9.02001100	-4.12948600	2.10087200
C	-9.51183900	-3.64446900	0.17229100
H	-9.89243100	-4.58762700	-0.24721000
C	-9.34407800	4.24619600	1.23796700
H	-10.25509300	4.36533400	0.63190900
N	10.06694500	-2.80064000	-0.03279000
N	8.40789800	4.70666900	-1.42597100
N	-10.02273900	-3.08712900	1.20360300
H	-10.80745700	-3.63215400	1.56463000
N	-9.05557600	5.02511800	2.21333500
H	-9.77467700	5.74002000	2.33434800
C	9.66605200	4.90310600	-1.36419300
H	10.38624700	4.14982500	-1.01611500

H	10.06297000	5.86612800	-1.68436500
C	10.41963500	-3.99347800	-0.30496600
H	9.79146900	-4.87342200	-0.10865400
H	11.39207600	-4.16154600	-0.76766800

Total electronic Energy (E_{total}) = -1965.622170 (Hartree/Particle).

Table S2. DFT-optimized geometry of **(2) TPA-TPA-COOH** (doublet) **(*COOH) model-b**, computed at the UB3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	-5.63547000	-0.11606600	-0.22191500
C	-6.43843100	-1.20116900	0.22549100
C	-7.22085900	-1.07642700	1.37704200
C	-6.44459700	-2.41346000	-0.49021900
C	-8.01640700	-2.14625400	1.81205900
H	-7.22500300	-0.15250600	1.94457700
C	-7.22092000	-3.48213100	-0.04777200
H	-5.83746100	-2.50629000	-1.38456800
C	-8.01049100	-3.35402700	1.09787800
H	-7.21941800	-4.41313900	-0.60666300
C	-4.31746200	-0.36680600	-0.67251800
C	-3.80312700	0.29528800	-1.80795700
C	-3.49239000	-1.28931400	0.00492000
C	-2.51760700	0.04181900	-2.24760500
H	-4.42809300	1.00765200	-2.33633300
C	-2.21078400	-1.55601600	-0.43981200
H	-3.87236500	-1.78765700	0.89088300
C	-1.67341000	-0.89986100	-1.58639900
H	-2.14424700	0.55560700	-3.12939800
H	-1.59240200	-2.25442200	0.11367900
C	-6.15423600	1.20091100	-0.21740900
C	-7.49821600	1.44222100	-0.54757200
C	-5.32719300	2.29143100	0.12045900
C	-7.99724800	2.74127600	-0.53308600
H	-8.14443300	0.61174600	-0.80984600
C	-5.83039900	3.58414400	0.11891100
H	-4.29176200	2.10970200	0.38796200
C	-7.17675500	3.83264200	-0.20726500
H	-9.04002300	2.91135000	-0.79084800
H	-5.19583400	4.42270300	0.38615400
H	-8.62113100	-4.18684100	1.43669100
C	-0.36822300	-1.12249900	-2.06673700
H	0.05735800	-0.47699500	-2.82908200
N	0.52725300	-2.07953800	-1.53125700
C	1.79488800	-1.59001400	-1.07208900
C	2.99801200	-2.23040300	-1.39595900

C	1.82618400	-0.40745100	-0.32292500
C	4.20927300	-1.69464400	-0.97119800
H	2.98527700	-3.14577200	-1.97459500
C	3.03891800	0.12364700	0.10859700
H	0.89498000	0.08541700	-0.06248900
C	4.24767400	-0.51416200	-0.20971900
H	5.13800000	-2.19196800	-1.22972800
H	3.05206900	1.03347800	0.69900000
N	5.48579200	0.02313200	0.22673000
C	5.70336500	1.42515700	0.17873200
C	6.49683900	-0.83734900	0.72741700
C	6.32538000	2.08880200	1.24888500
C	5.28056400	2.17646800	-0.93089800
C	7.84401800	-0.59049300	0.43127300
C	6.15919200	-1.93537400	1.53904500
C	6.54846200	3.46149500	1.19674200
H	6.63037900	1.52163600	2.12217100
C	5.46862900	3.55410400	-0.96351900
H	4.79020000	1.67453400	-1.75840400
C	8.84554600	-1.44127600	0.91409200
H	8.12614300	0.25890100	-0.18053600
C	7.16167000	-2.76998100	2.02980900
H	5.11976600	-2.12014800	1.78688300
C	6.13423300	4.21369700	0.08245700
H	7.00562000	3.96102500	2.04570000
H	5.12812900	4.13688300	-1.81345900
C	8.50499700	-2.53503900	1.72860000
H	6.89245500	-3.60329800	2.67240900
H	9.28396600	-3.16514700	2.14558800
C	-8.85076600	-2.02413200	3.02483500
H	-9.41217500	-2.93284100	3.28846800
C	-7.73232800	5.19402500	-0.20758600
H	-8.80233700	5.25217100	-0.45909700
N	10.18444100	-1.12451800	0.58396300
N	6.30320400	5.61093000	-0.02000900
N	-8.91299500	-0.94641900	3.71040300
H	-9.53881300	-1.05576300	4.51013500
N	-7.02848600	6.22999700	0.06307400
H	-7.59424300	7.07862700	0.01244500
C	7.36921500	6.15987000	0.41281300
H	8.21887800	5.60128400	0.82916300
H	7.45918900	7.24458000	0.36051100
C	10.98246700	-2.05380000	0.23614700
H	10.68148700	-3.10490400	0.12675200
H	12.02133100	-1.80219100	0.02305600
C	0.26334800	-3.43669400	-1.50423700
O	0.95718400	-4.28256100	-0.96475200
O	-0.88293600	-3.74224800	-2.16827300
H	-0.99179400	-4.70088700	-2.07226600

Total electronic Energy (E_{total}) = -2154.787956 (Hartree/Particle).

Table S3. DFT-optimized geometry of **(2′) *COOH′** (doublet) **model-c**, computed at the UB3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
N	6.06744200	0.27880000	0.04948300
C	6.73052000	0.79867100	1.19197800
C	7.72962400	0.06065400	1.83486100
C	6.37536100	2.06487100	1.69621700
C	8.38296200	0.58053700	2.96145400
H	8.01323000	-0.91993600	1.46944600
C	7.01114300	2.57278500	2.82685900
H	5.59879500	2.63660600	1.19934500
C	8.01763400	1.84009200	3.46063300
H	6.72771900	3.54997000	3.20644800
C	4.66034100	0.46631200	-0.07813000
C	4.10892600	0.90759700	-1.28906400
C	3.81031900	0.21547700	1.00965700
C	2.73064600	1.08179400	-1.40586000
H	4.76042700	1.10045900	-2.13510300
C	2.43603000	0.41059500	0.89101500
H	4.23435300	-0.13090000	1.94683200
C	1.88033000	0.83839000	-0.32034200
H	2.31535000	1.42506900	-2.35012800
H	1.77731100	0.20822100	1.72778600
C	6.78272200	-0.41267500	-0.95339300
C	8.09206900	-0.03375400	-1.29705600
C	6.18840400	-1.49638200	-1.63348700
C	8.78361600	-0.72701900	-2.28566000
H	8.56210700	0.79929800	-0.78627500
C	6.88155200	-2.17255400	-2.62651900
H	5.18131400	-1.80084700	-1.36982900
C	8.19475000	-1.80138000	-2.97095000
H	9.79590900	-0.41940200	-2.53794200
H	6.42473500	-3.01040500	-3.14296600
H	8.51795700	2.24205400	4.33778700
C	0.38190400	1.08341500	-0.46242000
H	0.10761200	0.93277200	-1.51526900
N	-0.37934100	0.23278100	0.43421200
C	-1.69882800	0.12460000	0.24690100
C	-2.40539800	-0.74597600	1.14700600
C	-2.49194700	0.78599900	-0.75686700
C	-3.76334500	-0.94316000	1.05709600
H	-1.82258200	-1.23616700	1.92022500
C	-3.85377900	0.58379200	-0.84030700
H	-2.02336700	1.45456000	-1.47032700
C	-4.52417900	-0.28253200	0.05780300
H	-4.26536500	-1.59821300	1.76075900
H	-4.42441100	1.08823700	-1.61284200
N	-5.90883400	-0.47897500	-0.03737300
C	-6.76260200	0.57442600	-0.47359000

C	-6.48969700	-1.73446700	0.30099100
C	-7.76750400	0.32313400	-1.41929800
C	-6.60641100	1.87462100	0.03287700
C	-7.67193900	-1.77800700	1.04841600
C	-5.89808100	-2.92969200	-0.14097100
C	-8.61618600	1.34597100	-1.83256400
H	-7.87683400	-0.67575400	-1.82889300
C	-7.43162200	2.90333300	-0.40816800
H	-5.82743000	2.07305500	0.76162000
C	-8.24942700	-3.00824300	1.38617000
H	-8.14895700	-0.86180000	1.37799900
C	-6.48678900	-4.15107800	0.18197600
H	-4.99614400	-2.89130200	-0.74200000
C	-8.46723300	2.64846300	-1.32228500
H	-9.37170300	1.14517300	-2.58600600
H	-7.30402600	3.91308900	-0.03183700
C	-7.65793400	-4.20337900	0.94119800
H	-6.03837300	-5.07177500	-0.17943800
H	-8.13231300	-5.15509900	1.15794500
C	9.44302800	-0.18867200	3.64343400
H	9.86536600	0.30334300	4.53243500
C	8.95002600	-2.50827700	-4.01424400
H	9.97213700	-2.13155400	-4.17339700
N	-9.44938300	-2.98302200	2.13325200
N	-9.27492700	3.73220300	-1.72546500
N	9.83755500	-1.33392100	3.23231500
H	10.57424500	-1.70519500	3.83452800
N	8.46232600	-3.48478600	-4.68666400
H	9.14418400	-3.83940300	-5.35904700
C	-10.52779200	3.56671400	-1.88931400
H	-11.05045100	2.62244400	-1.68330500
H	-11.12639500	4.40624500	-2.24159500
C	-9.60531400	-3.79657900	3.10033000
H	-8.83159600	-4.50267000	3.43201400
H	-10.55068800	-3.79337500	3.64240400
C	0.10947800	2.57737500	-0.20843100
O	-0.16756700	3.38061000	-1.07565200
O	0.22367400	2.91192200	1.09451800
H	0.05291300	3.86665600	1.16167300

Total electronic Energy (E_{total}) = -2154.777595 (Hartree/Particle).

Table S4. DFT-optimized geometry of **(3) TPA-TPA-CO** (singlet) **(*CO)**, computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	5.57461800	0.10423200	0.03018900

C	6.31268400	-1.06110000	-0.29283900
C	6.99602900	-1.15585000	-1.52207600
C	6.36351100	-2.14333500	0.60048500
C	7.71594600	-2.29798800	-1.84112500
H	6.95119600	-0.32652100	-2.22006600
C	7.07842800	-3.29059600	0.26623800
H	5.84230300	-2.08055000	1.54959500
C	7.76886900	-3.38779100	-0.95171500
H	7.11061600	-4.11912200	0.96998700
C	4.33117800	-0.01817600	0.71023600
C	4.02461400	0.81800700	1.79367300
C	3.39064100	-0.97764800	0.30213900
C	2.79960400	0.69839100	2.44711400
H	4.74342800	1.56527700	2.11292000
C	2.17929900	-1.10772200	0.97469800
H	3.61838600	-1.62119600	-0.54123700
C	1.86586300	-0.27020200	2.05476200
H	2.57571600	1.35810500	3.28158900
H	1.45825400	-1.85168000	0.64997900
C	6.07740500	1.38891200	-0.28901800
C	7.44816700	1.67194900	-0.17273900
C	5.20414900	2.40596100	-0.72510800
C	7.92839000	2.93874000	-0.49368300
H	8.12865400	0.89892500	0.16730400
C	5.69006700	3.66919000	-1.02990200
H	4.14529500	2.19092100	-0.82283800
C	7.06331900	3.95786000	-0.92152300
H	8.99222000	3.14265500	-0.39630700
H	5.01915600	4.45054500	-1.37149800
C	0.58249900	-0.40120600	2.80412800
H	0.25975800	0.50536100	3.32738500
N	-0.52211800	-1.22311700	2.20988900
C	-1.78113600	-0.91633200	1.65994800
C	-2.88403100	-1.73961200	1.92488700
C	-1.92070000	0.20214500	0.83067400
C	-4.12293500	-1.42836100	1.37280600
H	-2.76800500	-2.60241300	2.57287400
C	-3.16006200	0.49857600	0.26933300
H	-1.05728500	0.82494700	0.61709400
C	-4.27754400	-0.30967100	0.53572500
H	-4.98212600	-2.05481400	1.58753800
H	-3.26825000	1.36224600	-0.37798500
N	-5.54186300	-0.00339300	-0.03027000
C	-5.98259000	1.34411600	-0.09137500
C	-6.34870400	-1.04134500	-0.56271800
C	-6.61300000	1.83795700	-1.24545300
C	-5.77707400	2.21402000	0.99335900
C	-7.74227500	-1.03115500	-0.37811600
C	-5.77177600	-2.08834600	-1.30096300
C	-7.05397600	3.15691700	-1.30172000
H	-6.75004400	1.18240900	-2.09922700
C	-6.18344700	3.54194300	0.91972800
H	-5.28370900	1.84516100	1.88652100
C	-8.53363200	-2.03615200	-0.92334500
H	-8.19981900	-0.22238400	0.18178300
C	-6.56185500	-3.11414300	-1.81178000

H	-4.70105200	-2.08919700	-1.47712900
C	-6.85661200	4.02661400	-0.21368400
H	-7.51186100	3.52847300	-2.21364600
H	-6.01073900	4.21783200	1.75117900
C	-7.95540200	-3.11017800	-1.61975500
H	-6.10094400	-3.89823200	-2.40518100
C	7.59992500	5.28840600	-1.24601000
H	8.69065800	5.38304000	-1.13326400
N	-7.24959300	5.38167500	-0.21828600
N	6.85719500	6.25933800	-1.62924200
H	7.41387500	7.09682100	-1.80683300
C	-8.34772200	5.72860300	-0.76484600
H	-9.06255600	5.01946100	-1.20479800
H	-8.60902700	6.78607200	-0.79239000
H	-9.61109600	-2.01969500	-0.79383700
H	8.23702900	-2.37418800	-2.78979900
C	8.52118300	-4.61025200	-1.27337500
H	8.47525200	-5.39348900	-0.50151200
N	9.17741700	-4.75176400	-2.36447900
H	9.62952300	-5.66663100	-2.40251900
N	-8.81616000	-4.10062600	-2.13806200
C	-8.45512000	-5.32316400	-2.14623000
H	-9.11988700	-6.06374800	-2.58996300
H	-7.50979700	-5.68437600	-1.71803600
C	-0.00022700	-1.67197900	3.36032300
O	-0.09666200	-2.51130700	4.22214900

Total electronic Energy (E_{total}) = -2078.919291 (Hartree/Particle).

Table S5. DFT-optimized geometry of **(4) TPA-TPA-CHO** (doublet) **(*CHO)**, computed at the UB3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	5.79995900	0.09162600	0.07733200
C	6.62933800	-1.02892800	-0.17743000
C	7.57839300	-0.99255600	-1.21916600
C	6.50704000	-2.19535500	0.59494500
C	8.38697300	-2.09082100	-1.47257900
H	7.66805400	-0.09735600	-1.82544100
C	7.31463600	-3.29677900	0.32516100
H	5.77832500	-2.23367300	1.39726100
C	8.26832400	-3.26453100	-0.70430300
H	7.20911900	-4.19246700	0.93278900
C	4.44289800	-0.10489100	0.43644700
C	3.85238600	0.65666900	1.46610900
C	3.65827900	-1.06845900	-0.22994700
C	2.53094100	0.45430200	1.81686900

H	4.44503400	1.40335800	1.98422700
C	2.34110600	-1.28606100	0.12863100
H	4.10152500	-1.64794000	-1.03317700
C	1.72608800	-0.53321700	1.17208400
H	2.09776000	1.04526300	2.61949000
H	1.76827500	-2.03464400	-0.40300100
C	6.32766300	1.40376300	0.00541300
C	7.62198100	1.68310300	0.47415000
C	5.55471500	2.45102400	-0.53581400
C	8.12780100	2.97747700	0.39383500
H	8.22262400	0.88555300	0.89773300
C	6.06287400	3.74018900	-0.60082000
H	4.55721300	2.23719700	-0.90484800
C	7.36111700	4.02637200	-0.13800600
H	9.13069600	3.17885000	0.76323500
H	5.47149500	4.54553500	-1.02386600
C	0.38153700	-0.67532400	1.57271500
H	-0.05652300	0.05216900	2.24890400
N	-0.52168700	-1.65430000	1.12010500
C	-1.86043800	-1.22704500	0.84321800
C	-2.96218400	-1.88692300	1.40333400
C	-2.07579200	-0.11681500	0.01576500
C	-4.25725000	-1.45760900	1.12240900
H	-2.80665600	-2.71589900	2.08672800
C	-3.36820600	0.31383800	-0.26451500
H	-1.22335100	0.39199000	-0.42340900
C	-4.47931600	-0.35332800	0.28278000
H	-5.10408900	-1.96797900	1.56819700
H	-3.52460300	1.16626400	-0.91659700
N	-5.79545100	0.08262000	-0.00044000
C	-6.08470300	1.47050100	-0.09217300
C	-6.82964400	-0.86663600	-0.21403000
C	-6.90353400	1.95952500	-1.12255700
C	-5.54619800	2.37742200	0.83614100
C	-8.11139100	-0.65843100	0.32278600
C	-6.59684900	-2.01560900	-0.98756300
C	-7.19996700	3.31704300	-1.20622500
H	-7.30192400	1.26928200	-1.85906100
C	-5.81153100	3.73828000	0.72752500
H	-4.90665600	2.00969300	1.63179900
C	-9.13186300	-1.57333600	0.08669400
H	-8.30415500	0.23253600	0.91108900
C	-7.60882300	-2.94978200	-1.18958500
H	-5.61991000	-2.16765200	-1.43492400
C	-6.66717400	4.22583700	-0.27394200
H	-7.81046300	3.68157100	-2.02697400
H	-5.38237400	4.44174800	1.43380300
C	-8.88976500	-2.74820000	-0.64388000
H	-7.41921500	-3.81670300	-1.81551900
C	7.92152100	5.38451500	-0.20307600
H	8.94972800	5.47497900	0.17907500
N	-6.90094100	5.61634300	-0.32262500
N	7.26606000	6.38273500	-0.66745600
H	7.82560400	7.23612200	-0.62913900
C	-8.05296500	6.06109700	-0.63828000
H	-8.92340800	5.41942100	-0.83330100

H	-8.19790400	7.13863500	-0.71002100
C	-0.22236100	-3.01166200	1.06074900
H	-1.04639200	-3.58845300	0.60781200
O	0.81875000	-3.52097300	1.43717700
H	-10.12630500	-1.40517800	0.48755800
H	9.11336200	-2.06675200	-2.27823300
C	9.11075000	-4.44254100	-0.96039900
H	8.91118000	-5.30082200	-0.30101000
N	10.00535800	-4.46822800	-1.87740100
H	10.48036200	-5.37199700	-1.89798400
N	-9.96720200	-3.63779800	-0.83928400
C	-9.76780200	-4.89671500	-0.83167600
H	-10.60808300	-5.56243700	-1.02652500
H	-8.79265000	-5.35983400	-0.62647900

Total electronic Energy (E_{total}) = -2079.541733 (Hartree/Particle).

Table S6. DFT-optimized geometry of **(5) TPA-TPA-OCH_2** (singlet) **(*OCH_2)**, computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	-5.32258000	0.01441700	-0.23027100
C	-6.37693800	-0.89573900	0.05901600
C	-7.05087200	-0.83160500	1.28156800
C	-6.74765000	-1.86918000	-0.88767700
C	-8.09693200	-1.72289000	1.56164400
H	-6.77701300	-0.09108100	2.02483100
C	-7.77383500	-2.76709700	-0.60185200
H	-6.22463500	-1.91595000	-1.83712100
C	-8.45401800	-2.69638700	0.61647000
H	-8.05161900	-3.51518800	-1.33823500
C	-4.13815300	-0.46350600	-0.84634600
C	-3.50976800	0.27743200	-1.85937900
C	-3.57874300	-1.69271000	-0.44918200
C	-2.34402900	-0.20219300	-2.45446400
H	-3.93444200	1.22528900	-2.17190100
C	-2.42436200	-2.16764500	-1.05969900
H	-4.05483800	-2.26333300	0.34118200
C	-1.79162900	-1.42821400	-2.06847500
H	-1.86716700	0.38117800	-3.23847500
H	-1.98622800	-3.10814500	-0.74079000
C	-5.46284700	1.38733000	0.08833800
C	-6.69804500	2.03562300	-0.07199500
C	-4.36436100	2.12186800	0.57857800
C	-6.82647600	3.38272000	0.25482800
H	-7.55100300	1.48071500	-0.44709400
C	-4.49808400	3.46762500	0.88786500

H	-3.41066400	1.62359300	0.71648600
C	-5.73399700	4.12264900	0.73278400
H	-7.78999600	3.87010300	0.12511000
H	-3.65411200	4.03158000	1.27122100
H	-9.25988700	-3.39258900	0.83360800
C	-0.55417100	-1.94922100	-2.73191900
H	-0.09191000	-1.16651600	-3.35861300
N	0.43278600	-2.64955500	-1.89043300
C	1.58549600	-2.04474300	-1.38747600
C	2.76817800	-2.78466700	-1.21110800
C	1.57051500	-0.68986400	-1.00691800
C	3.90669200	-2.18033200	-0.68267200
H	2.79909200	-3.83391100	-1.49008100
C	2.70681200	-0.09932400	-0.46135800
H	0.65965600	-0.10907700	-1.11282300
C	3.88999600	-0.83321700	-0.29765500
H	4.81789900	-2.75677400	-0.55793000
H	2.68516200	0.94482000	-0.16562200
N	5.05507200	-0.21836200	0.24878900
C	5.50492200	1.01170500	-0.28954500
C	5.74021000	-0.84916500	1.31426700
C	6.01312300	2.02197400	0.54631600
C	5.41302000	1.26288700	-1.67010800
C	7.13909100	-0.79044100	1.39951300
C	5.02222800	-1.54526400	2.30505500
C	6.45235800	3.22941000	0.01314500
H	6.05612500	1.85603200	1.61759900
C	5.81706000	2.48594500	-2.19491600
H	5.00786700	0.49867300	-2.32479000
C	7.81718400	-1.43262900	2.44200300
H	7.71427600	-0.25356200	0.65389100
C	5.70230800	-2.16752400	3.35021800
H	3.93962700	-1.58146500	2.25535000
C	6.37453900	3.47590200	-1.37005500
H	6.81391900	4.00582700	0.68087900
H	5.73200800	2.68299600	-3.25891400
C	7.09548400	-2.11890900	3.43410700
H	5.13532300	-2.68102500	4.12159900
H	7.61659000	-2.57157200	4.27145600
C	-8.81932000	-1.66097100	2.84850600
H	-9.60386700	-2.42252900	2.97087100
C	-5.89978400	5.54623600	1.06264100
H	-6.91909100	5.93487600	0.91602500
N	9.22786800	-1.32061000	2.46636000
N	6.77633100	4.68691400	-1.97270800
N	-8.55124400	-0.79028000	3.74598700
H	-9.15380100	-0.90722300	4.56233700
N	-4.93587200	6.27592300	1.48673800
H	-5.25096500	7.23155400	1.66079700
C	7.80106200	5.31042600	-1.54027800
H	8.44995700	4.93792200	-0.73562400
H	8.06588200	6.26397800	-1.99643800
C	9.93478400	-2.34254500	2.74423100
H	9.51507700	-3.34193000	2.92468900
H	11.01792500	-2.23351100	2.79889200
O	-0.74164200	-3.17196000	-3.50137500

C	0.41933200	-3.73820900	-2.86872000
H	0.23080000	-4.73936500	-2.46278500
H	1.29838900	-3.75108200	-3.53559800

Total electronic Energy (E_{total}) = -2080.131203 (Hartree/Particle).

Table S7. DFT-optimized geometry of **(6) TPA-TPA-OCH_3** (doublet) **(*OCH_3)**, computed at the UB3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	-6.06629200	-0.02912700	-0.32314900
C	-6.56318000	-1.06335200	-1.15831500
C	-7.58367700	-1.91155800	-0.71593700
C	-6.01849800	-1.25224900	-2.44352200
C	-8.07143000	-2.93008200	-1.54730500
H	-8.01187900	-1.79102500	0.27280200
C	-6.48996700	-2.27618100	-3.26181200
H	-5.22496400	-0.59670000	-2.78602600
C	-7.51803000	-3.11443700	-2.82355500
H	-6.06097300	-2.41166000	-4.25023400
C	-4.66184500	0.21811800	-0.29011200
C	-4.16832100	1.52763600	-0.40284500
C	-3.75759700	-0.84253000	-0.15550500
C	-2.79644900	1.76089400	-0.37046000
H	-4.86513100	2.35295500	-0.50918700
C	-2.38227500	-0.60095900	-0.14161300
H	-4.13564700	-1.85629900	-0.06731900
C	-1.88504500	0.70182500	-0.24522600
H	-2.41974100	2.77470400	-0.47192400
H	-1.68127000	-1.42082100	-0.03837100
C	-6.93852600	0.74946900	0.46836500
C	-8.22454000	1.08536500	0.00971700
C	-6.52777800	1.21233100	1.73632900
C	-9.07166600	1.85242800	0.80328600
H	-8.55470700	0.74158400	-0.96421100
C	-7.37534100	1.98719300	2.51414800
H	-5.54010900	0.95290000	2.10174400
C	-8.66599500	2.32108300	2.06296500
H	-10.06287000	2.10197400	0.43138200
H	-7.05922900	2.33538900	3.49202900
H	-7.88985400	-3.90761900	-3.46692100
C	-0.39372100	1.02207600	-0.21967400
H	-0.19292200	1.66225600	0.65442800
N	0.39620900	-0.18534300	-0.14126400
C	1.72225000	-0.08167700	-0.02910000
C	2.46008600	-1.31254600	0.07564100
C	2.49840400	1.13300300	0.00923300

C	3.82823900	-1.33686800	0.21403900
H	1.89108000	-2.23565600	0.02865400
C	3.86868700	1.10031600	0.15330500
H	1.99613400	2.08764500	-0.08208800
C	4.56914900	-0.12764900	0.25893000
H	4.35213400	-2.28428000	0.27977200
H	4.42644200	2.03002900	0.19421500
N	5.96360100	-0.14529100	0.40006800
C	6.76806400	0.85667900	-0.21417800
C	6.60454500	-1.16772700	1.15634600
C	7.80407500	1.46993200	0.50565800
C	6.53251900	1.24466300	-1.54291900
C	7.77273400	-1.76681900	0.67192500
C	6.08622800	-1.55465400	2.40355000
C	8.60541400	2.43434700	-0.09840400
H	7.97475100	1.18810400	1.53954900
C	7.31096200	2.23407700	-2.13349600
H	5.72925700	0.77519400	-2.10110000
C	8.40850800	-2.77348200	1.40915100
H	8.19361300	-1.46257900	-0.27985800
C	6.73307700	-2.54385700	3.14224700
H	5.19525000	-1.06983100	2.78732900
C	8.37712000	2.82054300	-1.43176200
H	9.38573600	2.92175800	0.47808600
H	7.12245400	2.54828900	-3.15490500
C	7.89048500	-3.15782100	2.65822400
H	6.34167300	-2.82508500	4.11544000
H	8.41086100	-3.90064800	3.25422200
C	-9.15225100	-3.82674500	-1.09106900
H	-9.43528700	-4.60654100	-1.81402500
C	-9.58287700	3.13398100	2.87321200
H	-10.56790700	3.30741500	2.41311800
N	9.59071300	-3.33025700	0.86960600
N	9.13415900	3.81331100	-2.08808300
N	-9.71353900	-3.70545200	0.05201800
H	-10.43422600	-4.41723000	0.18318300
N	-9.26634100	3.60489600	4.02295400
H	-10.03987400	4.13866400	4.42234800
C	10.39710200	3.86304100	-1.92543100
H	10.96487800	3.13336000	-1.33176200
H	10.95728500	4.66336100	-2.40805300
C	9.77148000	-4.58980000	0.91758600
H	9.03060500	-5.29583100	1.31740000
H	10.70466800	-5.00167300	0.53403900
O	-0.04291400	1.88361900	-1.32321200
C	-0.15901600	1.28479700	-2.61282100
H	0.54062700	0.44814200	-2.73242000
H	-1.17959500	0.92610900	-2.80066000
H	0.08585800	2.06872700	-3.33280600

Total electronic Energy (E_{total}) = -2080.727035 (Hartree/Particle).

Table S8. DFT-optimized geometry of **(7) TPA-TPA-O** (singlet) **(*O)**, computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
N	-5.92780300	-0.30820800	-0.34277600
C	-6.85722400	-1.35149800	-0.07530200
C	-7.89162100	-1.15793300	0.84424500
C	-6.73930500	-2.58823600	-0.73686700
C	-8.81391600	-2.18318300	1.09953600
H	-7.99634500	-0.21349500	1.36661500
C	-7.64358000	-3.61360100	-0.46871300
H	-5.93648300	-2.73605600	-1.45153400
C	-8.68362200	-3.41629800	0.44301100
H	-7.54309900	-4.56468200	-0.98292900
C	-4.54696600	-0.61391200	-0.44992900
C	-3.75775300	-0.01492900	-1.44433800
C	-3.95228300	-1.53118500	0.43677400
C	-2.40214200	-0.32345300	-1.54083600
H	-4.20926600	0.68882200	-2.13515800
C	-2.60304900	-1.84460700	0.32474000
H	-4.55737900	-1.99249700	1.21004200
C	-1.81206200	-1.24008400	-0.66323400
H	-1.80328300	0.14543600	-2.31787800
H	-2.14319600	-2.54901100	1.00992900
C	-6.38411300	1.02121000	-0.51564700
C	-7.59116400	1.28161000	-1.18447800
C	-5.63488600	2.10390500	-0.01242600
C	-8.03484800	2.59205000	-1.33867300
H	-8.17730700	0.45705400	-1.57520900
C	-6.07791300	3.40736800	-0.18338400
H	-4.70787800	1.90881100	0.51614200
C	-7.28829400	3.67514200	-0.84972100
H	-8.97207400	2.77658800	-1.85859100
H	-5.50455200	4.24024400	0.21014900
H	-9.39263500	-4.21503600	0.64443000
C	-0.36778500	-1.55906100	-0.77861900
H	0.15600400	-1.07791700	-1.60945600
N	0.41266400	-1.76998300	0.42714800
C	1.80535400	-1.42094600	0.34215300
C	2.70746500	-1.99443000	-0.55951400
C	2.24843800	-0.45699500	1.25528700
C	4.03965500	-1.58379000	-0.56255900
H	2.36239400	-2.75769900	-1.24750900
C	3.58001300	-0.05105400	1.25154300
H	1.54750500	-0.04317600	1.97373100
C	4.49219700	-0.60896300	0.34020000
H	4.74020500	-2.02663400	-1.26283600
H	3.92277900	0.69511300	1.96051500
N	5.85227000	-0.19946100	0.34038500
C	6.17429100	1.17660600	0.46664400

C	6.88305800	-1.16649700	0.21979500
C	7.24214400	1.58905100	1.28107200
C	5.41610800	2.15352200	-0.20105700
C	8.02326300	-0.89298100	-0.54758200
C	6.77821400	-2.40350700	0.88119800
C	7.56445400	2.93776600	1.39697800
H	7.81583900	0.84536700	1.82427400
C	5.71497700	3.50364900	-0.05148100
H	4.58246600	1.84742200	-0.82423700
C	9.03822300	-1.84834500	-0.67888800
H	8.12999600	0.05984500	-1.05366100
C	7.79890300	-3.34467500	0.75999200
H	5.90687100	-2.61227700	1.49212000
C	6.81251600	3.91609800	0.72121800
H	8.37604100	3.23816200	2.05300500
H	5.11938800	4.25868600	-0.55466200
C	8.93230300	-3.08138000	-0.01245900
H	7.71847600	-4.28825000	1.29208300
H	9.74154400	-3.80204200	-0.07127300
C	-9.91412800	-1.98762400	2.06547200
H	-10.56037000	-2.86649600	2.20828300
C	-7.77994100	5.04860100	-1.03519500
H	-8.74958700	5.12243600	-1.55084200
N	10.16480000	-1.49866200	-1.46017700
N	7.06767500	5.30047600	0.81946900
N	-10.09756700	-0.88340400	2.68390800
H	-10.90429900	-0.94174100	3.30757400
N	-7.13248000	6.07722400	-0.62975400
H	-7.63847200	6.93660300	-0.84942400
C	8.26764900	5.72867100	0.86254900
H	9.15130400	5.08148700	0.77524100
H	8.43900800	6.79836600	0.98007700
C	10.65937200	-2.35093000	-2.26664100
H	10.23087900	-3.34854100	-2.43569500
H	11.55105500	-2.08280400	-2.83316700
O	0.06444300	-2.87986100	-0.51084400

Total electronic Energy (E_{total}) = -2040.769125 (Hartree/Particle).

Table S9. DFT-optimized geometry of **H_2** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
H	0.00000000	0.00000000	0.37139700
H	0.00000000	0.00000000	-0.37139700

Total electronic Energy (E_{total}) = -1.178539 (Hartree/Particle).

Table S10. DFT-optimized geometry of **CO_2** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16949100
O	0.00000000	0.00000000	-1.16949100

Total electronic Energy (E_{total}) = -188.590582 (Hartree/Particle).

Table S11. DFT-optimized geometry of **CO** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
C	0.00000000	0.00000000	-0.64984200
O	0.00000000	0.00000000	0.48738200

Total electronic Energy (E_{total}) = -113.317323 (Hartree/Particle).

Table S12. DFT-optimized geometry of **H_2O** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
O	0.00000000	0.00000000	0.11647900
H	0.00000000	0.76944100	-0.46591800
H	0.00000000	-0.76944100	-0.46591800

Total electronic Energy (E_{total}) = -76.434058 (Hartree/Particle).

Table S13. DFT-optimized geometry of **CH_3OH** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
C	0.04651200	0.66772600	0.00000000
H	1.09377600	0.97908200	0.00000000
H	-0.43959200	1.08149600	0.89506000
H	-0.43959200	1.08149600	-0.89506000
O	0.04651200	-0.75925900	0.00000000
H	-0.86575800	-1.07435900	0.00000000

Total electronic Energy (E_{total}) = -115.735996 (Hartree/Particle).

Table S14. DFT-optimized geometry of **CH_4** (singlet), computed at the B3LYP-D3/ 6-31+G** level in absence of any solvent.

Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
H	0.63098700	0.63098700	0.63098700
H	-0.63098700	-0.63098700	0.63098700
H	-0.63098700	0.63098700	-0.63098700
H	0.63098700	-0.63098700	-0.63098700

Total electronic Energy (E_{total}) = -40.526296 (Hartree/Particle).

Table S15. Calculated total electronic energy (**E_{total}**), correction of zero-point energy (**E_{ZPE}**), entropy effect (**TS**), and enthalpy effect (**$\int C_P dT$**), and Gibbs free energy (**G**) of species in the reaction.

No.	Species	E_{total} (eV)	E_{ZPE} (eV)	TS (eV)	$\int C_P dT$ (eV)	G (eV)
1	*	-53487.331117	17.520849	3.361879	18.661415	-53454.5107
2	*COOH	-58634.796986	18.208971	3.576478	19.435334	-58600.7292
2′	*COOH′	-58634.515049	18.210576	3.615227	19.440777	-58600.4789
3	*CO	-56570.304395	17.779820	3.522615	18.970672	-56537.0765
4	*CHO	-56587.241913	18.075798	3.503764	19.273617	-56553.3963
5	*OCH_2	-56603.282217	18.447588	3.500390	19.635964	-56568.6991
6	*OCH_3	-56619.495640	18.694586	3.562243	19.914609	-56584.4487
7	*O	-55532.184968	17.625205	3.440204	18.787485	-55499.2125
	H_2 (g)	-32.069696	0.276849	0.402512	0.366755	-31.8286
	CO_2 (g)	-5131.813763	0.314591	0.661122	0.412035	-5131.7483
	CO (g)	-3083.523003	0.136574	0.610685	0.226508	-3083.7706
	H_2O (g)	-2079.877726	0.579358	0.583107	0.682217	-2079.1993
	CH_3OH (g)	-3149.338482	1.392843	0.735504	1.509090	-3147.1721
	CH_4 (g)	-1102.777251	1.217601	0.575117	1.321331	-1100.8134

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