A triazole-based covalent organic framework as a photocatalyst toward visible-light-driven CO_2 reduction to CH_4

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Materials: All reagents and solvents were obtained from commercial suppliers and used as received: dichloromethane (DCM), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), ethanol, glacial acetic acid, 4-Fromyl phenyl boronic acid, dimethyl acetamide and o-dichlorobenzene (*o*-DCB) were obtained from Spectrochem Pvt. Ltd. n-butyl alcohol (*n*-BuOH), was purchased from Sigma-Aldrich Chemical Co. Ltd. 3,5-Diamino-1,2,4-triazole (TRZ) and 1,3,5-Tribromobenzene were purchased from TCI chemicals. All the photophysical studies were carried out using HPLC grade solvents. $^{13}CO_2$ cylinder was purchased from Sigma-Aldrich Chemical Co. Ltd.

General instrumentation and methods: ^{1}H NMR spectra were recorded on Bruker AVANCE-400 spectrometer (at 400 MHz) with chemical shifts recorded as ppm, and all spectra were calibrated against tms. Powder X-ray diffraction patterns for the COF was recorded using Rigaku smartLab diffractometer having Cu-Kα radiation source (α = 0.15406 nm) operating at a voltage and current 60 kV and 60 mA, respectively. Bruker FT-IR spectrometer was used to record infrared

spectra. Solid-state Cross-Polarization Magic Angle Spinning (CP/MAS) ^{13}C NMR spectrum was recorded on a Bruker AVANCE NEO 400M spectrometer at 25 ℃. N_2 (77 K) and CO_2 (195, 273, and 298 K) adsorption measurements were carried out in a QUANTACHROME IQ2. Samples were degassed at 250 °C and 1×10^{-1} Pa vacuum for 12 h before performing adsorption isotherm measurement. Mettler Toledo-TGA 850 instrument was used to measure the thermal stability in N_2 atmosphere within the temperature range 30-800 °C at a heating rate of 5 °C/min. Morphological studies have been carried out using Bruker Leica-S440I Field Emission Scanning Electron Microscope (FE-SEM) by placing samples on a silicon wafer under high vacuum with an accelerating voltage of 100 kV. Transmission Electron Microscopy (TEM) analysis has been performed using JEOL JEM-3010 with an accelerating voltage at 300 kV. 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 carbon-coated copper grid prior to TEM analysis. AFM imaging of the samples were carried out using Asylum Research MFP-3D Origin AFM in tapping mode using AC160TS silicon probes, with nominal tip radii <10 nm. UV-vis studies were performed using Perkin Elmer Model Lambda 900 spectrophotometer instrument. The photoluminescence properties were performed in Fluorolog 3.21 spectrofluorimeter (Horiba Jobin-Yvon) instrument. Quantum yield calculations were carried out using calibrated integrated sphere attached with the Edinburgh FLS 980 spectrophotometer. The excited state lifetime studies were carried out using Edinburgh instrument (FLS 1000). For the lifetime measurement, a nano-LED source of 405 and 510 nm were used. The lamp profile was collected by placing a scatterer (Ludox AS40 colloidal silica, Sigma-Aldrich) in place of the sample. The decays were analyzed using IBH-DAS-6 decay

analysis software. Goodness of fits was evaluated from the χ^2 criterion and visual inspection of the residuals of the fitted functions to the data. Mean (average) fluorescence lifetimes (τ_{avg}) for bi-exponential iterative fittings were calculated from the decay times (τ_1 and τ_2) and the normalized pre-exponential factors (a_1 and a_2), using the following relation:

$$\tau_{avg} = a_1\tau_1 + a_2\tau_2$$

Femtosecond transient absorption (TA) experiments were performed using a pump-probe setup (CDP Corporation, Russia) described earlier.[1] Briefly, 800 nm laser pulse (50 fs, 1 kHz) from an amplified laser system (Amplified Technologies, France) was used for the generation of the 400 nm light that was used to excite the sample (pump) using a BBO crystal. A broad white light, generated by focusing a low energy 800 nm laser pulse onto a calcium fluoride plate was used to probe the pump induced changes in the optical absorbance of the sample. The samples were dispersed in acetonitrile using a mechanical shaker for 1 h. The large dispersed particles were removed with the help of a centrifuge. The samples were taken in a 1 mm thick optical cell and rotated during the experiment to avoid sample decomposition. All transient spectra were recorded at least twice to check the reproducibility of the data.

Electrochemical characterization:

Mott-Schottky and impedance measurement were carried out with a CHI760E workstation (CHI Instruments, USA) via a conventional three-electrode system in 0.2 M Na_2SO_4 aqueous solution.

Preparation of working electrode for Mott-Schottky and impedance measurement: 2.5 mg of **TFPB-TRZ** COF was dispersed in a solution of 250 µL water, 250 µL isopropyl alcohol (IPA) and 10 µL of nafion to prepare a homogenous slurry. Subsequently, 12 µL of slurry coated on glassy carbon electrode and then dried in room temperature. The Ag/AgCl electrode was employed

as the reference electrode, and Pt plate was used as the counter electrode, respectively. During impedance measurement, a white LED lamp (LEICA KL1600 LED) was used for illumination.

Preparation of working electrode for transient photocurrent: 2.5 mg of **TFPB-TRZ** COF was dispersed in a solution of 250 µL water, 250 µL isopropyl alcohol (IPA) and 10 µL of nafion to prepare a homogenous slurry. Subsequently, 300 µL of slurry was coated on ITO glass plate (1 cm × 1 cm) and then dried at room temperature. The Ag/AgCl electrode was employed as the reference electrode, and Pt plate was used as the counter electrode respectively. The transient photocurrent responses were carried out under visible-light irradiation conditions (300 W Xenon arc lamp).

***In-situ* diffuse reflectance FT-IR (DRIFT) measurement:** In-situ diffuse reflectance FT-IR measurement was carried out by FT-IR spectrometer (BRUKER Vertex 70V) with a designed reaction cell equipped with ZnSe window. The catalyst was spin-coated over a glass slide and placed in the center of the designed reaction cell. A high vacuum pump was used to pump out all the gases from the reaction cell. Then pure CO_2 (99.99%) gas and H_2O vapor were passed into the reactor for 5 minutes. At last, visible light was turned on, and the IR signal was *in-situ* collected through MCT detector with 4 cm^{-1} resolution and 128 scan along with the reaction.

Photocatalytic CO_2 reduction: The stock solution was prepared by dispersing 3 mg of finely powdered COF sample in 30 ml water and sonicated for 30 minutes. Similarly, another stock solution has also been prepared for control studies in which 3 mg catalyst was dispersed in 30 ml of water containing 10 µM 1-benzyl-1,4-dihydronicotinamide (BNAH) as a sacrificial electron donor. 7 ml of catalyst containing stock solution was taken in a Quartz tube cell with 30 ml volume. In another set of experiment 6 ml of catalyst and BNAH containing stock solution was taken and 1 ml of triethylamine (TEA) was added to the reaction mixture as a base and sealed the setup making a total volume of 7 ml of the reaction mixture and 23 ml of void space. Highly pure CO_2

gas (99.99%) was purged into the reaction mixture for 30 minutes and was allowed to equilibrate in the CO_2/solvent system. A 300 W Xenon Arc lamp was used as the light source with a visible band pass filter (λ > 420 nm) for the photocatalytic reaction. During irradiation, 1 ml of gas production was continuously taken from the reaction cell at a given time interval and subsequent gas formation (CO and CH_4) was analyzed using gas chromatography Mass Spectrometry (SHIMADZU GC-2010 PLUS). Gaseous products were quantified by using RT® Molecular sieve 5A column (45 m, 0.32 mm ID, 30 μm df) with a mass detector. The calibration was done by a standard gas mixture of H_2, CO, CH_4 of different concentrations in ppm-level. Importantly, GC-MS has a detection limit of 1.0 ppm for H_2, CO and CH_4. After the photocatalysis, the reaction mixture was filtered to remove the residual solid, and the solution was further analyzed to determine the amount of liquid product. The liquid product was detected using RID detector in High-performance liquid chromatography (Agilent Infinity1260) with Hi-Plex H column (300 x 7.7 mm) and 5 mM H_2SO_4 aqueous solution as eluent. The liquid product was also verified with ^{1}H-NMR using the water suppression method. For $^{13}CO_2$ experiment, we purged the reaction mixture with $^{13}CO_2$ and estimated using Gas Chromatography-Mass Spectrometry (GC-MS) (Shimadzu Corp., Japan) equipped with the mass detector. Selectivity was calculated by using the following equation:

$$Selectivity_{CH4} = \frac{8 \times n_{CH_4}}{(2 \times n_{CO} + 8 \times n_{CH_4})}$$

Apparent Quantum Efficiency (AQE) measurement: For measuring the apparent quantum yield (AQY) of the reaction system, the monochromatic LED lamps with band pass filter of 350, 400, 450, 500, 550, and 600 nm were used as the light source. The reactions were conducted on the same photochemical experimental setup under the optimized reaction conditions. The

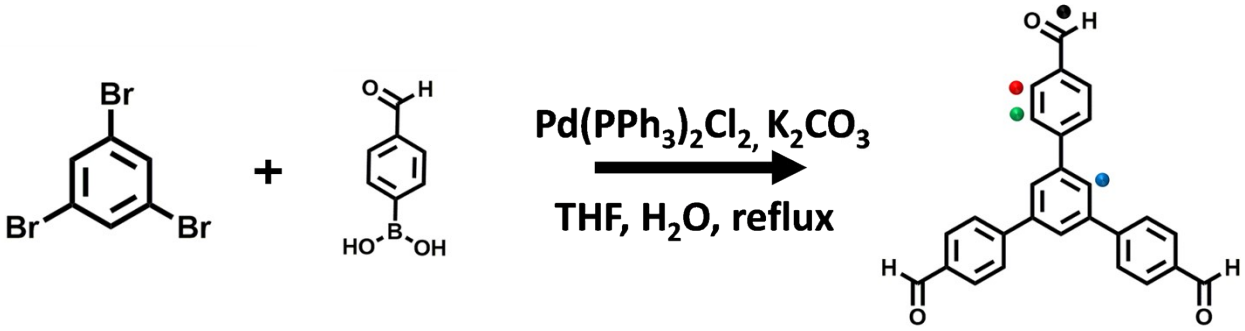
Newport-843-R was used to measure the intensity of incident monochromatic illumination (0.23, 0.114, 0.107, 0.20, and 0.33 mW cm^{-2}). The irradiated area for the reaction was controlled at 1.0×1.0 cm^2. Depending on the amount of CH_4 and CO produced by the photocatalytic reaction in 7.5 hours, and the AQY was calculated as follows:

$$AQY\% = 8\times[n(CH_4)\cdot N_A\cdot\hbar\cdot c)]\times 100\%/(I\cdot S\cdot t\cdot\lambda)$$

Where, N_A is Avogadro constant (6.022×10^{23}/mol), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^8 m/s), S is the irradiation area (cm^2), I is the intensity of irradiation light (W/cm^2), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Synthesis:

Synthesis of 1,3,5-Tris(4-formylphenyl)benzene (TFPB):



1,3,5-Tribromobenzene (500 mg, 1.59 mmol), (4-formylphenyl) boronic acid (953 mg, 6.35 mmol) and K_2CO_3 (1.68 g, 15.9 mmol) were dissolved in THF (30 ml), water (5 ml) and ethanol (10 ml). The solution was degassed three times, $Pd(PPh_3)_4$ (183.7 mg, 0.159 mmol) was added under an N_2 stream and the mixture was degassed three times again. The resulting solution was then heated at 90 °C for 48 h. The organic layer was then decanted and the aqueous layer was extracted two times using CH_2Cl_2. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel using n-hexane/EtOAc (10%) as the eluent to give the title compound TFPB as an off-white solid (465 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz,

ppm): d 10.04 (s, 3H), 7.97 (d, J ¼ 8.4 Hz, 6H), 7.95 (s, 3H), 7.84 (d, J ¼ 8.4 Hz, 6H). ESI HRMS calcd (M+) 390.13412, found 390.13011.

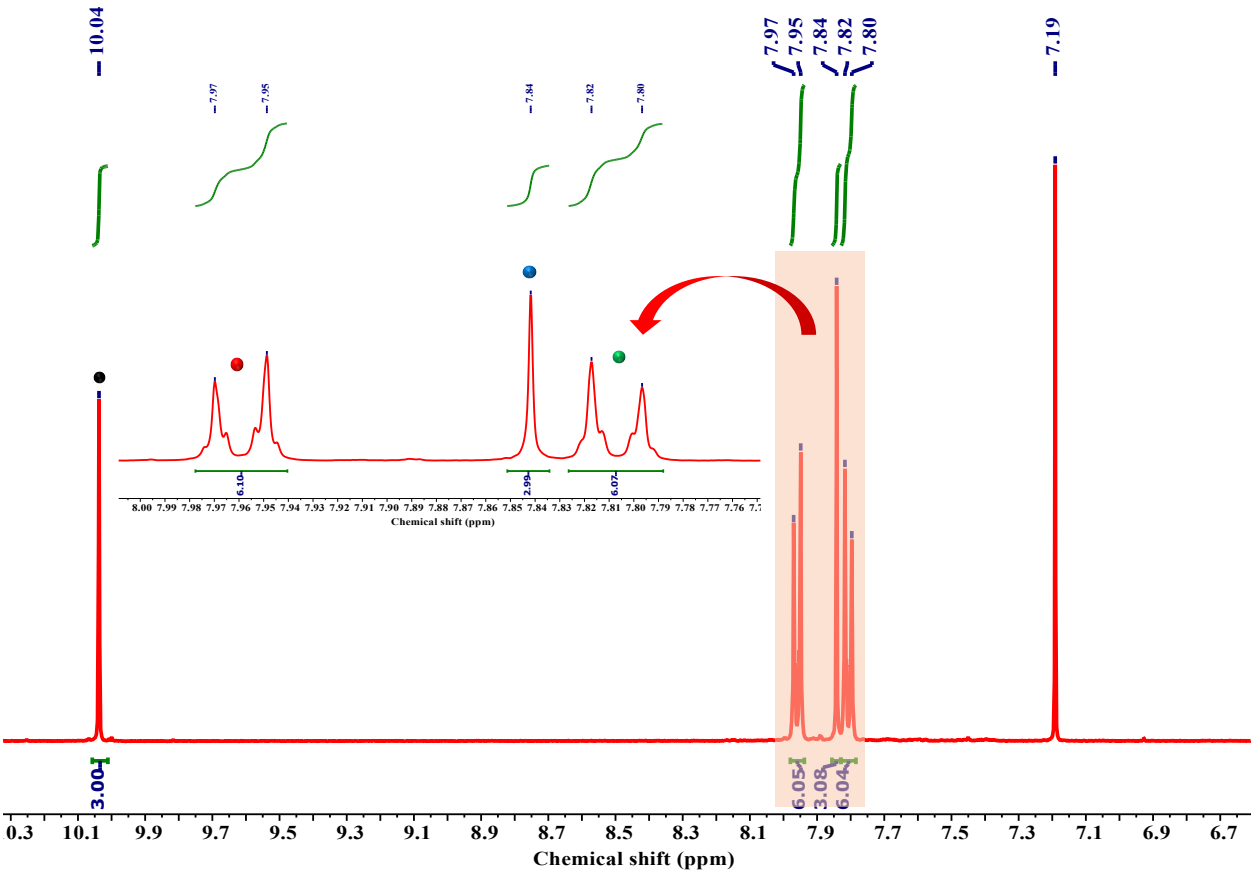


Figure S1: ^{1}H NMR of 1,3,5-tris(4-formylphenyl)benzene (TFPB).

Synthesis of TFPB-TRZ COF:

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was loaded with 1,3,5-Tris(4-formylphenyl)benzene (TFPB) (26.16 mg, 0.067 mmol) and 3,5-Diamino-1,2,4-triazole (TRZ) (9.9 mg, 0.1 mmol), n-BuOH (1.0 mL) and odichlorobenzene (O-DCB) (1.0 mL) and sonicated for 15 minutes. After 0.2 mL aqueous acetic acid (6 M) addition, the mixture was again sonicated for 10 minutes to afford a homogeneous dispersion. The tube was undergone three cycles of freeze-pump-thaw under liquid N_2 and 10^{-4} mbar internal pressure. Then it was sealed by a flame to a length of 10 cm,

approximately. The reaction was heated to 120 °C for 5 days yielding a yellow solid. The solid was isolated by filtration and washed with dry ethanol, dichloromethane and THF and dried at 60 °C for 3 h to obtain **TFPB-TRZ** COF.

Table S1: Synthesis of **TFPB-TRZ** COF under variable solvothermal conditions.

Sl. No.	Condition Reaction	Temp. (°C)	Time (Days)	Crystallinity
1	Dioxane/Mesitylene/6M AcOH (0.375/1.125/0.4 ml)	125	3	Amorphous
2	Dioxane/Mesitylene/DMAc/6M AcOH (1/1/0.33/0.33 ml)	120	3	Amorphous
3	Dioxane/Mesitylene/6M AcOH (1/1/0.2 ml)	120	3	Amorphous
4	Benzyl alcohol/Mesitylene/6M AcOH (900/100/100 µl)	120	3	Amorphous
5	o-DCB/n-BuOH/6 M AcOH (670/330/100 µl)	120	3	Amorphous
6	Dioxane/Mesitylene/6M AcOH (330/670/100 µl)	120	3	Amorphous
7	Dioxane/Mesitylene/6M AcOH (900/100/100 µl)	120	3	Amorphous
8	o-DCB/n-BuOH/6 M AcOH (500/500/100 µl)	120	3	Amorphous
9	Dioxane/Mesitylene/6M AcOH (330/670/100 µl)	120	3	Amorphous
10	Dioxane/Mesitylene/6M AcOH (1.5/1.5/0.5 ml)	120	8	Amorphous
11	Benzyl alcohol/Mesitylene/6M AcOH (900/100/100 µl)	120	3	Amorphous
12	o-DCB/n-BuOH/6 M AcOH (2/1/0.3 ml)	120	3	Amorphous
13	Dioxane/Mesitylene/6M AcOH (880/120/100 µl)	100	3	Amorphous

14	o-DCB/DMAc/6 M AcOH (500/500/100 µl)	120	3	Amorphous
15	Dioxane/Mesitylene/6M AcOH (880/120/100 µl)	120	3	Amorphous
16	o-DCB/n-BuOH/6 M AcOH (500/500/100 µl)	120	3	Amorphous
17	o-DCB/n-BuOH/6 M AcOH (1/1/0.2 ml)	120	3	**Crystalline**

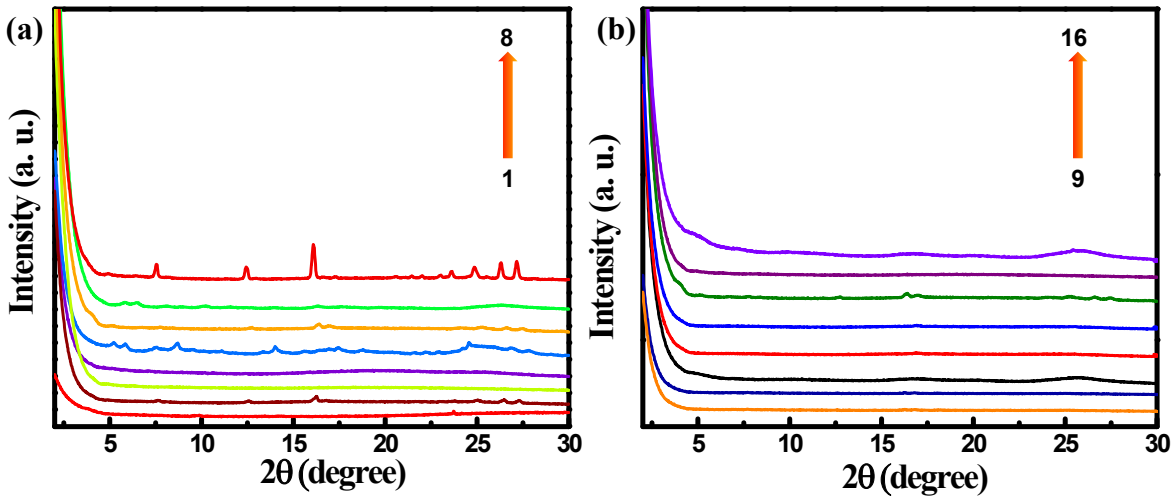


Figure S2: PXRD patterns of **TFPB-TRZ** synthesized under different solvent combination as described in **Table S1**. (a) For Sl. No. 1 to 8. (b) For Sl. No. 9 to 16, indicating amorphous polymer formation.

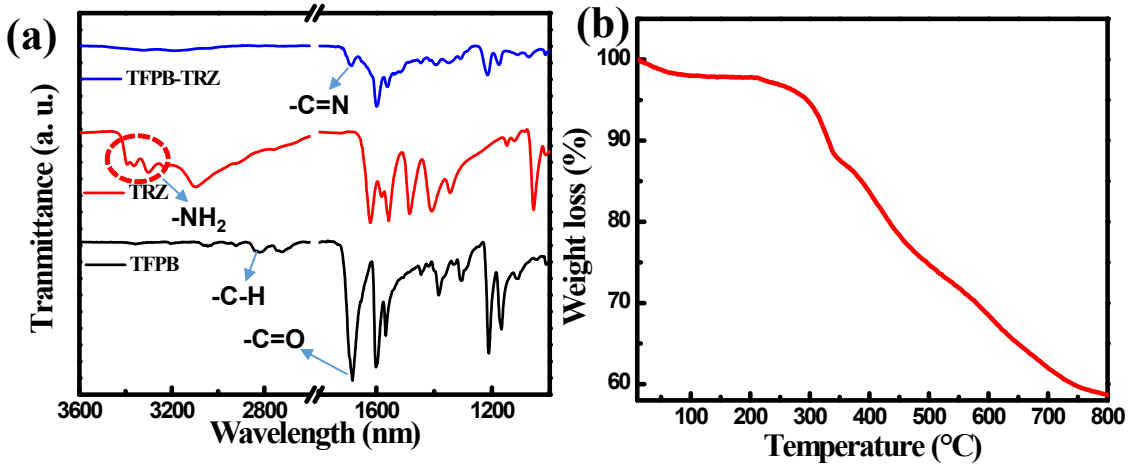


Figure S3: (a) FT-IR spectra of **TFPB-TRZ** COF, TFPB and TRZ ligand. (b) Thermogravimetric analysis (TGA) profile of **TFPB-TRZ** COF under N_2 atmosphere.

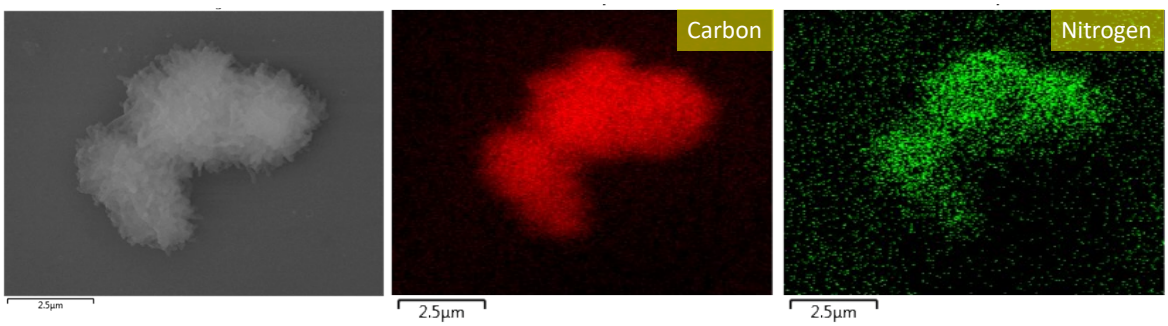


Figure S4: FE-SEM images of COF showing fibrous morphology. Elemental mapping of **TFPB-TRZ** COF showing uniform distribution of (b) carbon, and (c) nitrogen.

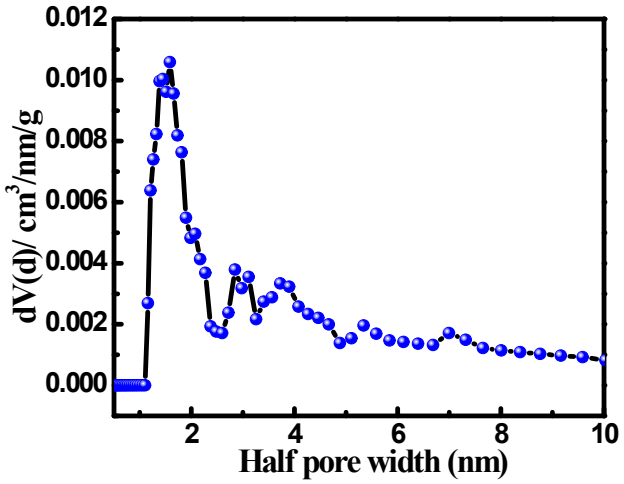


Figure S5: NLDFT pore size distribution plot obtained from N_2 adsorption-desorption analysis of the **TFPB-TRZ** COF.

Table S2: TDDFT analysis results for TFPB-imine fragment of **TFPB-TRZ** COF.

Experimental absorption maximum	Theoretical band	Transition	% Contribution	Assignment

400-480 nm (~440 nm)	**453.24 nm**	**HOMO → LUMO (c = 0.38120)**	**29 %**	**Extension of conjugation from TFPB core to imine group**

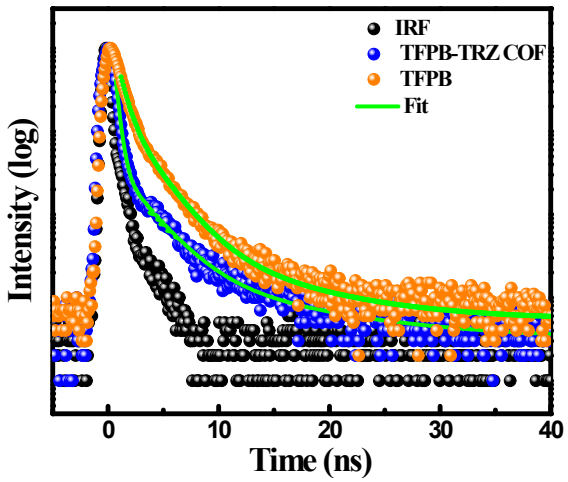


Figure S6: Time resolved luminescence decay curves of **TFPB-TRZ** COF and TFPB monomer building unit (λ_{ex} = 405 nm for COF, λ_{ex} = 340 nm for TFPB, λ_{em} = corresponding emission maxima). Green curves represent the fitting of the experimental curves.

Table S3: Summary of Time-resolved photoluminescence decay of TFPB ligand and **TFPB-TRZ** COF.

Compound	t_1 (ns)	t_2 (ns)	t_3 (ns)	B_1	B_2	B_3	τ_{avg} (ns)
TFPB Ligand	1.164 (39.08 %)	3.571 (52.81 %)	8.198 (8.12 %)	3574.144	1419.256	59.820	1.92
TFPB-TRZ COF	0.2037 (24.75 %)	2.432 (59.85 %)	10.20 (15.40 %)	757.128	242.004	15.639	0.88

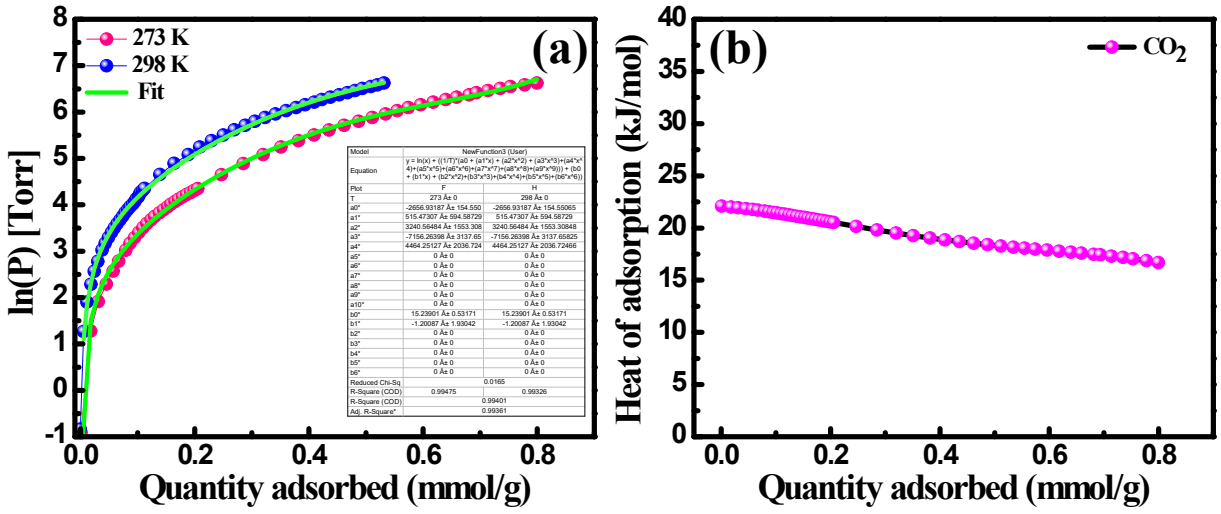


Figure S7: (a) Virial fitting parameters at two different temperature of CO_2 adsorption isotherm (c) CO_2 isosteric heat of adsorption calculated from 273 K and 298 K of **TFPB-TRZ** COF.

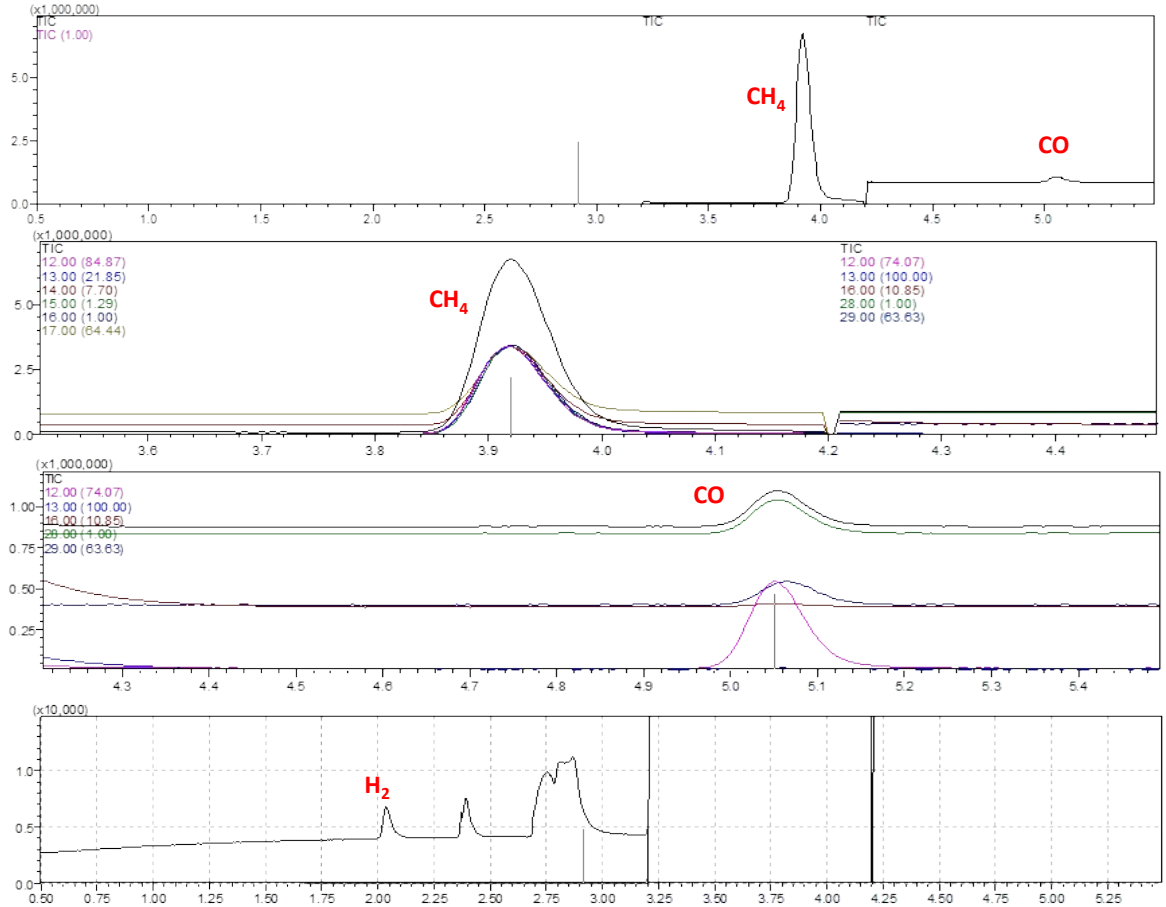


Figure S8: GC-MS Chromatogram showing different gaseous products (CH_4, CO and H_2). Plot at the below panels show mass of different fragment along with TIC (total integration count) plot. Bottom most panel: Zoom-in chromatogram showing the negligible evolution of H_2 during the photocatalytic CO_2 reduction in mixed solvent system under the influence of BNAH and TEA showing negligible amount of H_2 evolution.

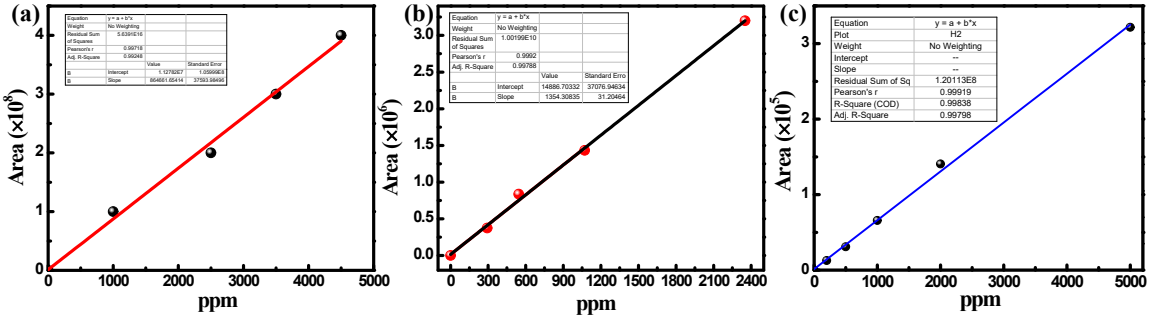


Figure S9. Calibration curve used for the quantification of (a) CH_4 (b) CO and (c) H_2 Calibration plot was obtained from standard concentration gas cylinders.

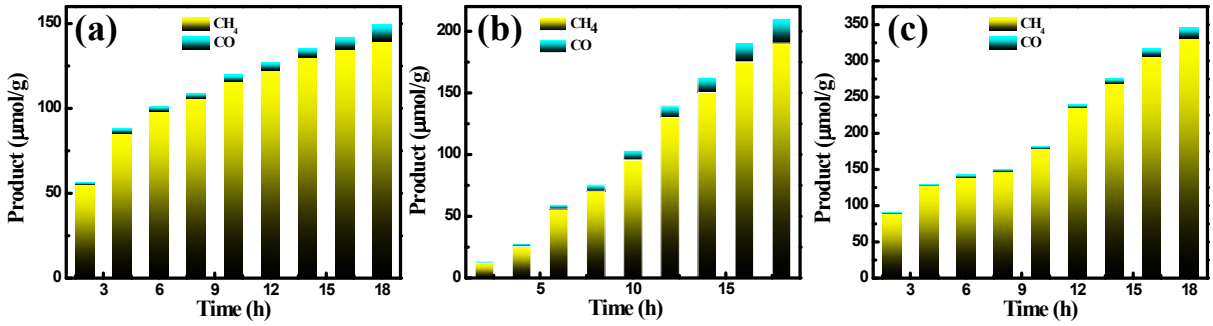


Figure S10: Photocatalytic evolution of CO and CH_4 using **TFPB-TRZ** COF (a) in aqueous medium without any sacrificial agents. (b) in ACN-H_2O mixture (2:1) in presence of TEA and (c) in aqueous medium under the combined influence of TEA and BNAH sacrificial agents in presence of visible light irradiation.

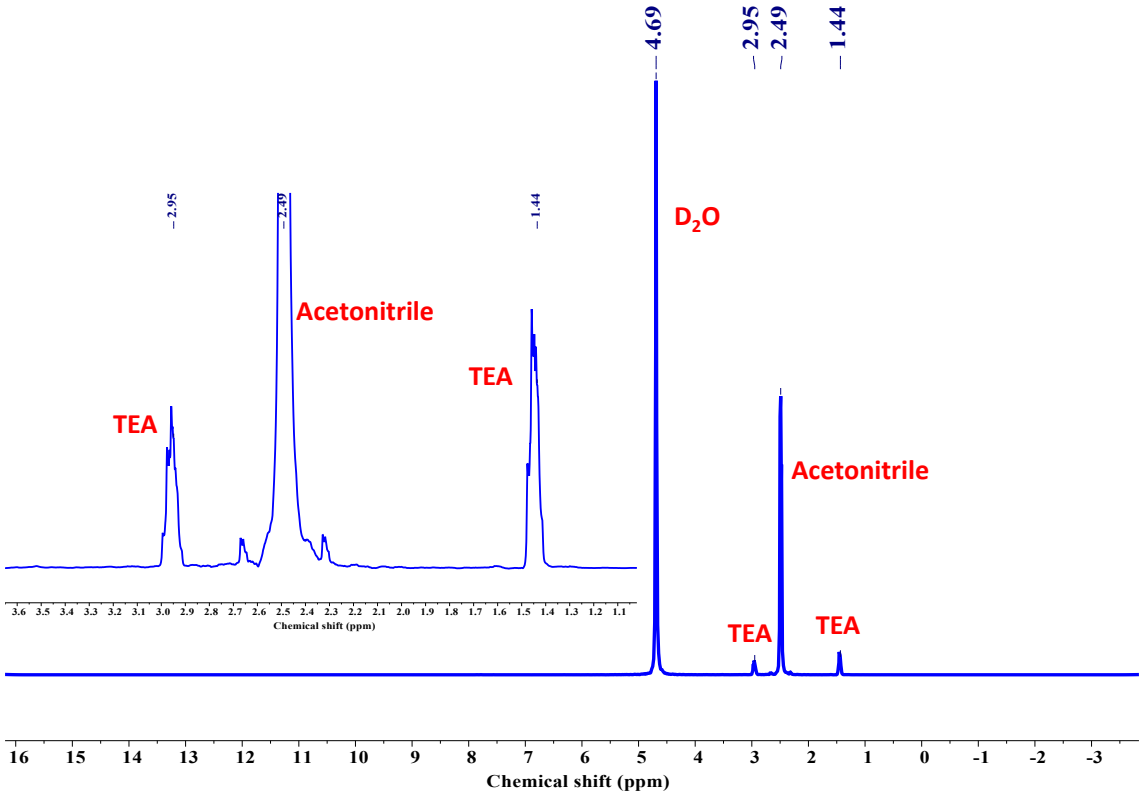
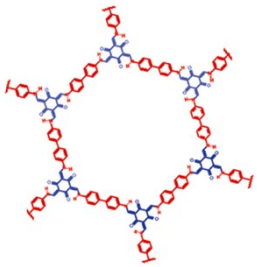
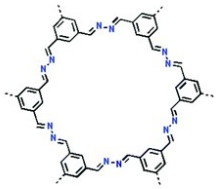
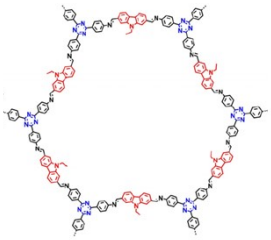
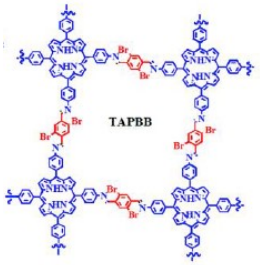
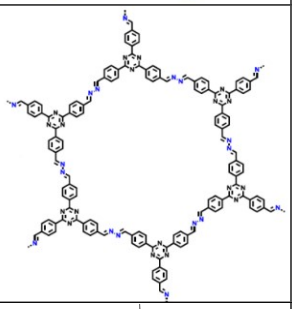
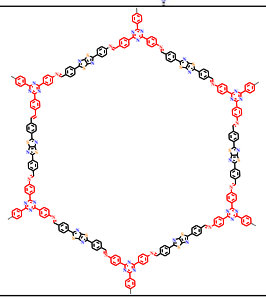
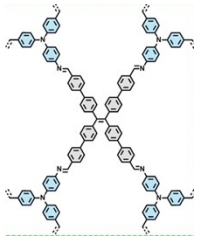
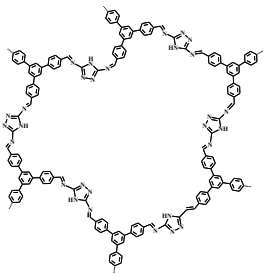


Figure S11: A representative ^{1}H NMR spectrum of liquid phase generated from CO_2 reduction catalyzed by **TFPB-TRZ** COF in ACN-H_2O medium in presence of BNAH and TEA. DMSO was used as an internal reference, and pre saturation method was implemented during experiment.

Table S4: Metal-free photocatalytic CO_2 reduction performance using COF-based porous organic polymers.

COFs	Chemical structure	Reaction medium and light source	Major Product (Maximum rate)	Selectivity	Reference
TpBD-X COF [X = -H_2, -$(CH_3)_2$, -$(OCH_3)_2$, and -$(NO_2)_2$].		10 : 1 (v/v) mixed solution of CH_3CN and TEOA 300 W Xe lamp with a UV-cut filter and an IR-cut filter (800 nm ≥ λ ≥ 420 nm)	(i) TpBD-H_2 COF: HCOOH (45.7 μmol h^{-1} g^{-1})	Not mentioned	*Catal. Sci. Technol., 2021, 11, 1717–1724*
			(ii) TpBD-$(CH_3)_2$ COF: HCOOH (86.3 μmol h^{-1} g^{-1})		
			(iii) TpBD-$(OCH_3)_2$ COF: HCOOH (108.3 μmol h^{-1} g^{-1})		
			(iv) TpBD-$(NO_2)_2$ COF: HCOOH (22.2 μmol h^{-1} g^{-1})		

ACOF-1		Water 500 W Xe lamp with a UV and an IR cut-off filter (800 nm ≥ λ ≥ 420 nm)	CH_3OH (0.36 μmol h^{-1} g^{-1})	~100	*Appl. Catal., B, 2018, 239,46-51*
CT-COF		H_2O vapour 300 W Xe lamp;Visible light (>420 nm)	CO (102.7 μmol h^{-1} g^{-1})	98	*Chemsuschem*, 2020, 13, 1725-1729
TAPBB-COF		Water (200≤ λ ≤1000 nm)	CO (24.6 μmol h^{-1} g^{-1})	95.6	*Chemsuschem*, 2020, 13, 2973-2980
N_3-COF		Water	CH_3OH (0.57 μmol h^{-1} g^{-1})	~100	*Appl. Catal., B, 2018, 239,46-51*
TTA-Tz COF		Water 300 W Xe lamp;Visible light (>420 nm)	CO (78 μmol g^{-1} h^{-1}) $Yield_{CO}$=2.8 mmol g^{-1}	**~99**	*ACS Catal.* 2023, 13, 9, 5926–5937
TT-COF		20:1 Acetonitrile:Water Triethylamine 300 W Xe lamp;Visible light (>420 nm)	CO (6.45 mmol g^{-1}) H_2 (0.561 mmol g^{-1}) CH_4 (0.195 mmol g^{-1})	83 CO selectivity	*J. Mater. Chem. A, 2023, 11, 13615-13622*

TFPB-TRZ		4:2 Acetonitrile:Water Triethylamine 300 W Xe lamp;Visible light (>420 nm)	**CH_4 (2.3 mmol g^{-1})** **CO (0.195 mmol g^{-1})**		This work

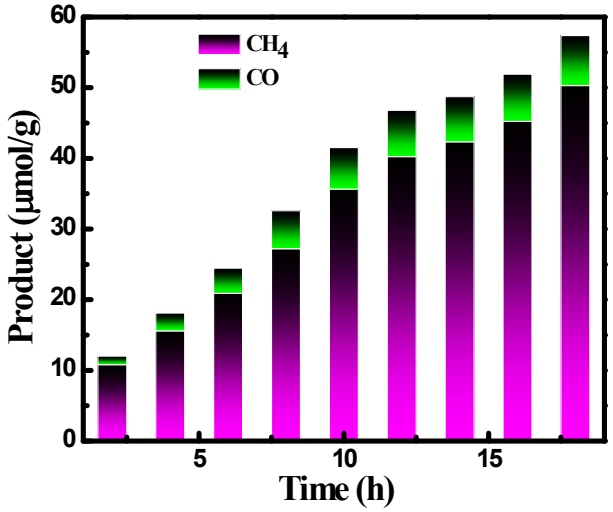


Figure S12: Photocatalytic evolution of CO and CH_4 using **TFPB-TRZ** COF in ACN-H_2O mixture (2:1) in presence of BNAH under visible light irradiation.

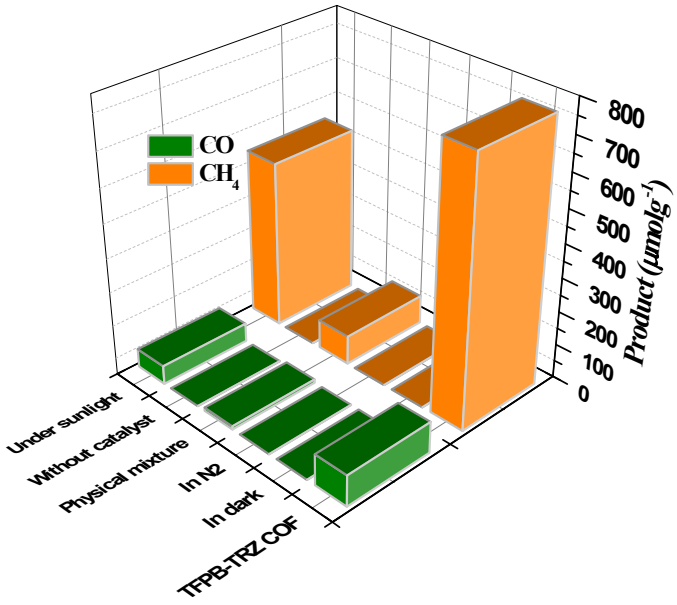


Figure S13: Photocatalytic CO_2 reduction carried out in different condition for 8 h of light irradiation.

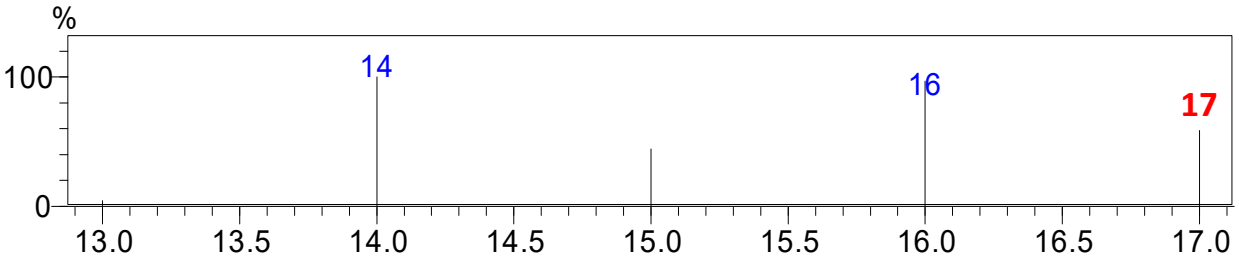


Figure S14: Mass spectra [m/z = 17] analysis of the carbon source of the generated CH_4 from the **TFPB-TRZ** COF promoted photocatalytic $^{13}CO_2$ reduction system in acetonitrile/water medium in presence of BNAH and TEA as sacrificial electron donor.

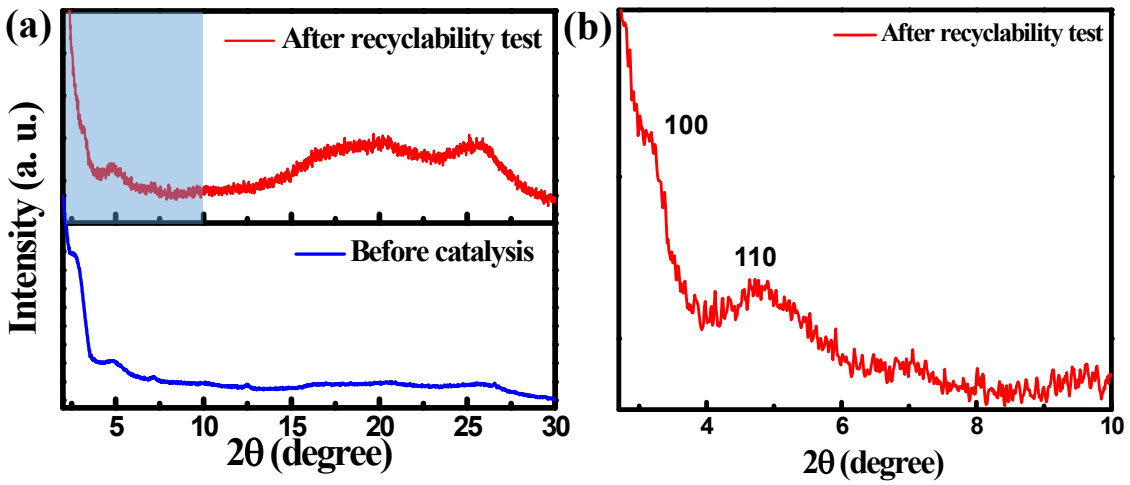


Figure S15: (a) PXRD pattern of the **TFPB-TRZ** COF recovered after performing five consecutive catalytic cycles. (b) Zoom-in PXRD pattern of the low angle region of the recovered catalyst.

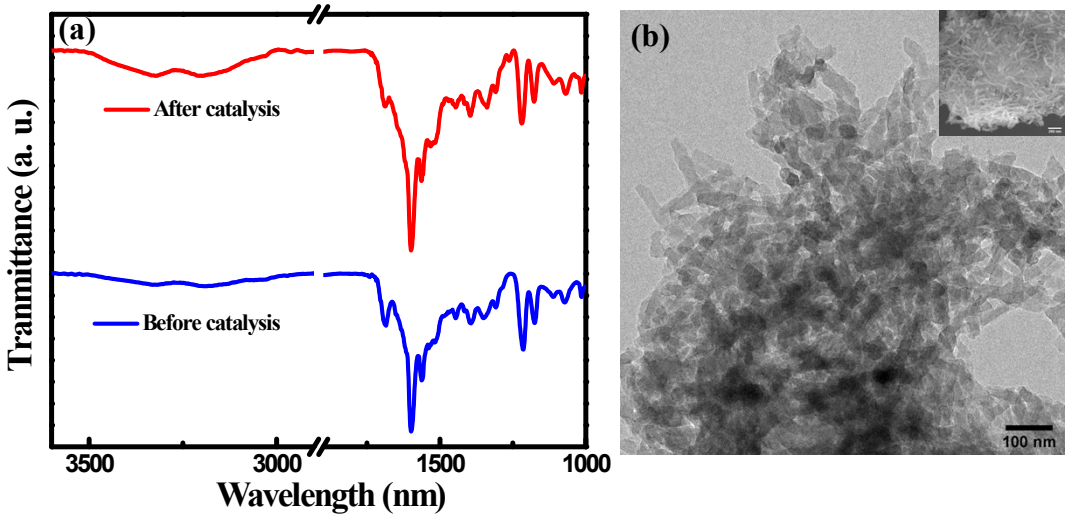


Figure S16: (a) FT-IR spectra of **TFPB-TRZ** COF before and after the photocatalytic cycle. (b) TEM images showing fibrillar morphology of the recovered sample after catalysis. Inset: SEM image of the post catalytic recovered sample showing similar entangled fibre like morphology which is in accordance with the TEM image.

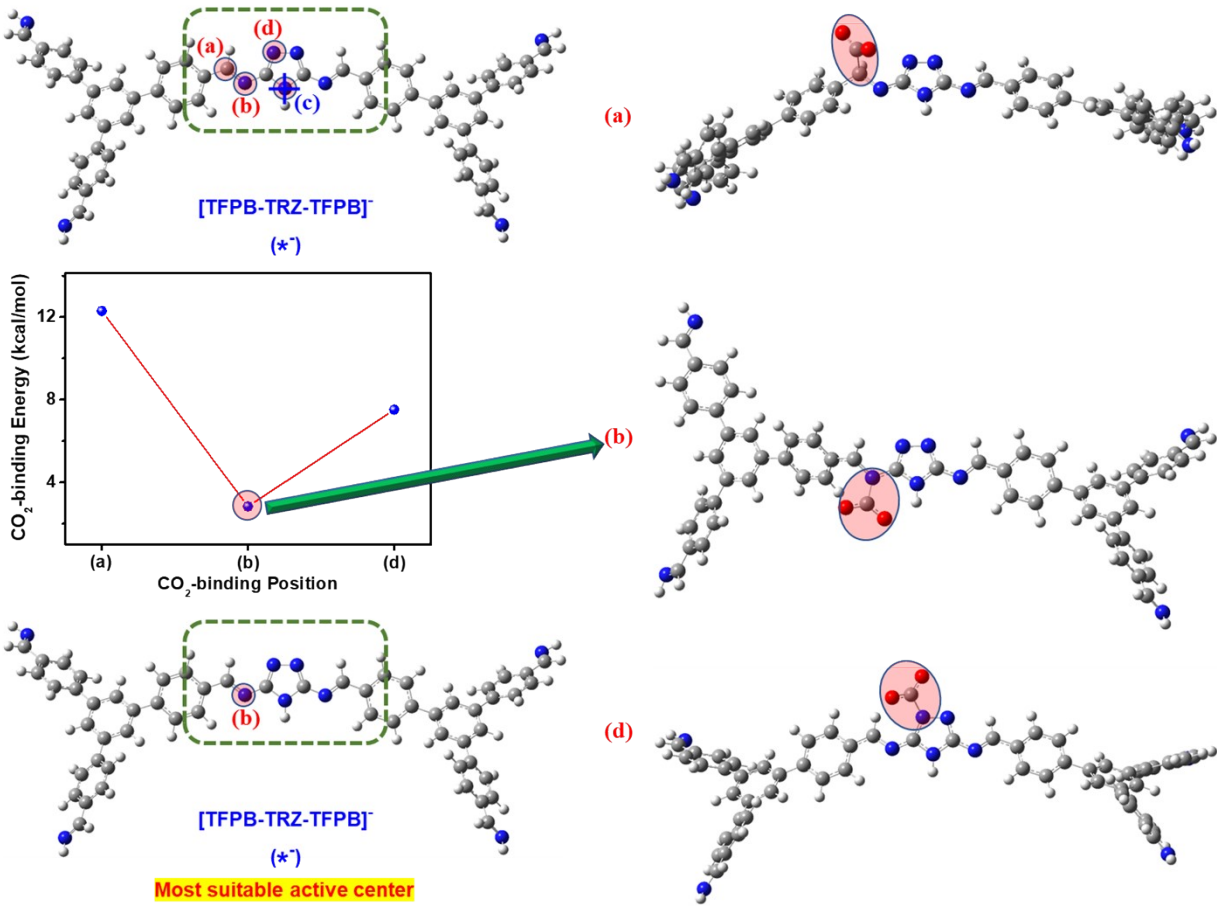


Figure S17: Identification of the most suitable active center for CO_2RR by CO_2-binding energy calculations considering different CO_2-bound models (model-**a** to model-**d**) with bound CO_2 on different potential CO_2-binding sites. The binding site marked in blue (**c**) was found to be incapable of CO_2-binding.

Computational Details:

Density functional theory (DFT) was used throughout the entire computation process in the Gaussian16 software package.[2] The geometry optimization and frequency calculations were performed utilizing B3LYP exchange-correlation functional along with 6-31+G** basis set for all atoms.[3-8] The implicit solvent effect of acetonitrile was incorporated into all computations by polarizable continuum model (PCM).[9] Grimme's d3 dispersion was also used to tackle weak interactions.[10] 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). For the transition state of the CO_2-binding step, the scan calculation and transition state calculation were also performed using the same level of theory. Time-dependent density functional theory (TDDFT) calculations were performed to assess the electronic absorption spectra. For TDDFT calculations, the same level of theory to that of optimization and frequency calculations, was used. 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 a concentration correction for c = 1 mol/ dm^3 condition in the solvent. The pictures of the optimized structures, molecular orbitals and spin density plots were taken from Gauss View 6.0.16.[11]

In **Figure S17**, the most suitable CO_2-binding site was identified through CO_2-binding energy calculations. The CO_2-binding energy calculations were performed on photo-reduced [TFPB-TRZ-TFPB]$^-$. The spin density distribution plot revealed that the unpaired electron in [TFPB-TRZ-TFPB]$^-$ intermediate is delocalized throughout the TFPB unit, imine bond and TRZ core (Table S6). Hence, multiple CO_2-bound models (model-**a** to model-**d**) were considered for computation by binding CO_2 on various potential active sites in [TFPB-TRZ-TFPB]$^-$ (**a-d**). However, DFT calculations revealed that center **c** (-NH- nitrogen atom of TRZ unit) could not bind CO_2. Thus, the binding sites **a**, **b** and **d** were left as the choices, among which the binding site **b** (imine nitrogen) was found to be the most suitable CO_2-binding site. Thus, we have proceeded with the mechanistic investigation of CO_2-to-CH_4 reduction by considering the imine nitrogen as the active site.

In **Figure S18**, full catalytic mechanism with possible side pathways for photocatalytic CO_2 reduction to CH_4 are reported along with their Gibbs free energy change (ΔG) values, which led us to select the most feasible catalytic cycle. A notable point in **Figure S18** is that the exergonic reduction step from *COOH to *$COOH^-$ intermediate (ΔG = -0.88 eV) is chosen as the main path over the highly endergonic *COOH to *CO^+ intermediate conversion step (ΔG = +1.99 eV). Additional point is that the intermediate *CH_3OH could not be stabilized in DFT calculation, which led the mechanistic pathway through *O intermediate rather than the *CH_3OH intermediate.

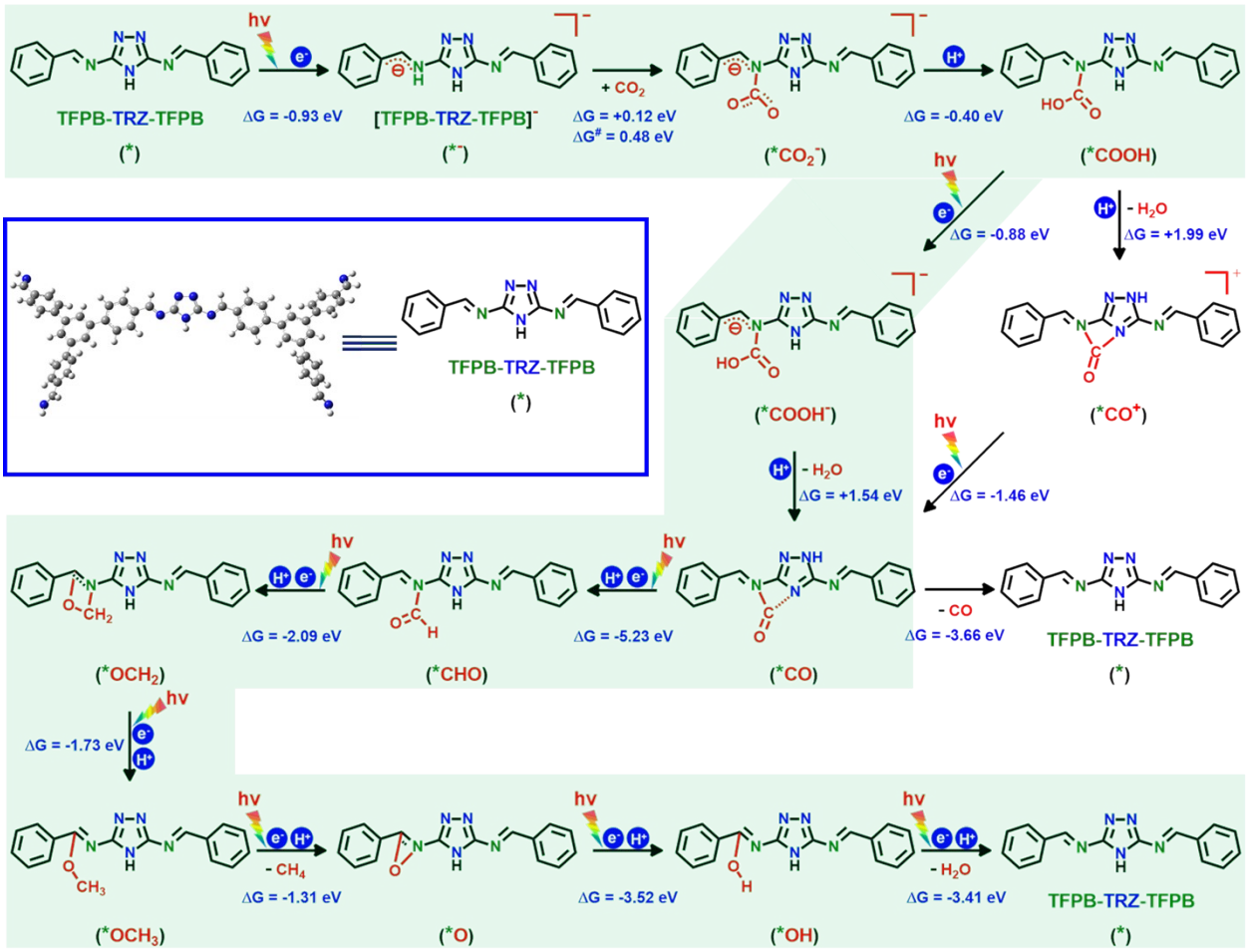


Figure S18: All the possible mechanistic pathways of photocatalytic CO_2-to-CH_4 reduction on TFPB-TRZ COF catalyst with respective ΔG values. Asterisk (*) denotes TFPB-TRZ-TFPB model, which represents TFPB-TRZ COF catalyst, adsorbed with intermediate species. The main mechanistic pathway is chosen based on thermodynamic feasibility, which is marked in green.

Cartesian coordinates of the computed structures

Coordinates are given in standard XYZ format

Table S5: DFT-optimized geometry of **TFPB-imine** (singlet), computed at the B3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	0.90305400	1.08501300	0.06502500
C	1.37313900	-0.23661900	0.06450100

C	0.48766100	-1.32460500	0.06502100
C	-0.89196600	-1.07090400	0.06465300
C	-1.39142600	0.23994800	0.06512600
C	-0.48190100	1.30789600	0.06468200
H	2.44265700	-0.42089800	0.06292200
H	-1.58634100	-1.90497100	0.06304600
H	-0.85703200	2.32627500	0.06314900
C	1.85279900	2.22640800	0.06653100
C	3.01956100	2.19319500	0.84798600
C	1.60730500	3.37271100	-0.71634700
C	3.90793400	3.26748800	0.84639200
H	3.21910300	1.33243900	1.47901200
C	2.49194800	4.44428400	-0.71862400
H	0.72447800	3.40748400	-1.34780800
C	3.65789200	4.40588700	0.06604400
H	4.80119200	3.22541200	1.46543900
H	2.30333200	5.32032500	-1.33034100
C	-2.85480100	0.49161000	0.06654000
C	-3.72454500	-0.29444400	-0.71630100
C	-3.40975100	1.51865900	0.84777900
C	-5.09491500	-0.06455000	-0.71867900
H	-3.31294300	-1.07633000	-1.34762800
C	-4.78434500	1.75045600	0.84604300
H	-2.76436800	2.12213900	1.47881400
C	-5.64502400	0.96434000	0.06579900
H	-5.75908000	-0.66622500	-1.33032800
H	-5.19483800	2.54507900	1.46489500
C	1.00143700	-2.71772900	0.06640900
C	2.11671300	-3.07801100	-0.71687700
C	0.38994500	-3.71173300	0.84820300
C	2.60290600	-4.37969100	-0.71917100
H	2.58766600	-2.33077300	-1.34868500
C	0.87663500	-5.01801000	0.84658100
H	-0.45501800	-3.45446300	1.47967300
C	1.98743400	-5.37039800	0.06589100
H	3.45573700	-4.65413900	-1.33121500
H	0.39414800	-5.77069500	1.46592200
C	4.61350300	5.52820900	0.08353600
H	5.48780700	5.37685900	0.73447700
C	-7.09479500	1.23036900	0.08326200
H	-7.40096200	2.06360600	0.73368900
C	2.48212000	-6.75887800	0.08350300
H	1.91397400	-7.44054600	0.73436200
N	4.43860200	6.59311600	-0.60447300
N	-7.92961600	0.54574200	-0.60408900
N	3.49215800	-7.13960400	-0.60422200
H	3.67897100	-8.13332700	-0.46017200
H	-8.88357200	0.88100600	-0.46020900
H	5.20597100	7.25154900	-0.46057800

Sum of electronic and thermal Free Energies = -1205.536262 (Hartree/Particle).

From TDDFT calculation in the absence of any solvent, $\boldsymbol{\lambda_{abs}}$ = 453.24 nm.

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

Atom	x	y	z
C	-8.86959100	-0.20283800	0.22568200
C	-9.81980300	-1.21275800	0.01278100
C	-11.16113700	-0.90455700	-0.25796700
C	-11.54493400	0.44360400	-0.31342400
C	-10.61734600	1.47478100	-0.10344400
C	-9.28259900	1.13648100	0.16368100
H	-9.51120000	-2.25228800	0.05658300
H	-12.57992100	0.69369300	-0.52335400
H	-8.55612900	1.92623700	0.32609300
C	-7.45396900	-0.54470600	0.51103900
C	-7.12631600	-1.61967600	1.35513800
C	-6.40080400	0.20110900	-0.05825400
C	-5.79698400	-1.93734600	1.62085500
H	-7.91879700	-2.19340700	1.82568500
C	-5.07442500	-0.11331200	0.20404100
H	-6.63245500	1.01902800	-0.73388200
C	-4.75028300	-1.19113500	1.05116800
H	-5.56408600	-2.76676700	2.28390600
H	-4.27025600	0.45897000	-0.24612600
C	-11.04083900	2.89674200	-0.16221100
C	-11.95126300	3.34016100	-1.14278500
C	-10.54582800	3.83548300	0.75797900
C	-12.35213900	4.66929000	-1.20224500
H	-12.32583500	2.63565900	-1.87949800
C	-10.94741800	5.16913200	0.69943200
H	-9.86327100	3.51401400	1.53883300
C	-11.85413800	5.60455400	-0.27818500
H	-13.04584700	5.00780800	-1.96474500
H	-10.55966100	5.87831400	1.42716900
C	-12.15538700	-1.98473600	-0.48045100
C	-11.82344700	-3.12900200	-1.23372200
C	-13.45111500	-1.89381200	0.05413500
C	-12.74924000	-4.14343400	-1.44496200
H	-10.83533700	-3.20673700	-1.67753700
C	-14.38069600	-2.91096100	-0.15700000
H	-13.72373600	-1.03448800	0.65926400
C	-14.04459200	-4.04760700	-0.90699000
H	-12.49208400	-5.01794400	-2.03344700
H	-15.37588300	-2.82558000	0.27332000
C	-3.36990800	-1.55616800	1.35309600
H	-3.22068000	-2.40767000	2.02680600
C	-12.26281300	7.02044100	-0.31714900
H	-11.80348200	7.65259200	0.45774000
C	-15.04659500	-5.10889100	-1.11463600
H	-16.02290600	-4.91726200	-0.64441000
N	-2.36368800	-0.91707500	0.85764700
N	-13.08659000	7.47611500	-1.18412300
N	-14.79833800	-6.16811000	-1.78858600

C	-1.09046400	-1.32188300	1.19262800
N	0.00001700	-0.68380900	0.66682400
N	-0.68309100	-2.29581600	1.99942700
C	1.09051200	-1.32187800	1.19254500
H	-0.00002000	0.09249000	0.02117400
N	0.68316400	-2.29584500	1.99936700
N	2.36370800	-0.91715400	0.85753700
C	3.36995000	-1.55611000	1.35310200
H	3.22070800	-2.40744300	2.02702800
H	-15.61448500	-6.78132600	-1.82027700
C	4.75028500	-1.19106900	1.05115400
C	5.07441900	-0.11346000	0.20374600
C	5.79701000	-1.93705500	1.62110700
C	6.40079000	0.20096600	-0.05855700
H	4.27023600	0.45864000	-0.24662800
C	7.12633400	-1.61938000	1.35538400
H	5.56410700	-2.76630600	2.28437100
C	7.45397100	-0.54462400	0.51100600
H	6.63242900	1.01870200	-0.73440900
H	7.91882200	-2.19292800	1.82614100
C	8.86958800	-0.20274500	0.22563300
C	9.28250000	1.13658500	0.16323400
C	9.81988200	-1.21266800	0.01311500
C	10.61724100	1.47489500	-0.10391500
H	8.55596100	1.92633600	0.32535100
C	11.16121200	-0.90446000	-0.25765000
H	9.51134400	-2.25220300	0.05723000
C	11.54490900	0.44371200	-0.31351100
C	11.04064300	2.89686400	-0.16310400
C	12.15555400	-1.98463400	-0.47973300
H	12.57989100	0.69381000	-0.52345800
C	10.54549400	3.83586600	0.75674700
C	11.95111600	3.34003600	-1.14374300
C	11.82372700	-3.12918800	-1.23261800
C	13.45126200	-1.89342700	0.05485500
C	10.94699700	5.16952200	0.69781200
H	9.86289700	3.51460000	1.53765100
C	12.35190600	4.66917400	-1.20359200
H	12.32579700	2.63533200	-1.88020700
C	12.74960400	-4.14362000	-1.44348300
H	10.83563900	-3.20715600	-1.67644000
C	14.38092800	-2.91057600	-0.15590400
H	13.72380600	-1.03388000	0.65970100
C	11.85376800	5.60469800	-0.27986900
H	10.55913400	5.87890800	1.42529400
H	13.04565200	5.00749600	-1.96614300
C	14.04493500	-4.04750700	-0.90551200
H	12.49253100	-5.01835300	-2.03167500
H	15.37609700	-2.82496700	0.27441300
C	12.26234900	7.02060100	-0.31924900
C	15.04702900	-5.10878100	-1.11277200
H	11.80293600	7.65296000	0.45542100
N	13.08613600	7.47606200	-1.18632500
H	16.02329800	-4.91693700	-0.64254500
N	14.79886000	-6.16826700	-1.78633400
H	15.61504000	-6.78145300	-1.81775400

H	-13.24339700	8.47632100	-1.04946600
H	13.24286900	8.47632000	-1.05197100

Sum of electronic and thermal Free Energies = -2650.923223 (Hartree/Particle).

From TDDFT calculation in the absence of any solvent, λ_{abs} = 415.88 nm.

Table S7: DFT-optimized geometry of **TFPB-TRZ-TFPB (*)** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.86806100	-0.19531500	0.23386000
C	-9.79654700	-1.22226500	0.00367100
C	-11.13700000	-0.93597200	-0.29607300
C	-11.54257100	0.40586800	-0.36316400
C	-10.63583300	1.45247900	-0.13618800
C	-9.30099600	1.13758100	0.16009400
H	-9.47162600	-2.25602100	0.05742700
H	-12.57683300	0.63815100	-0.59471300
H	-8.59169300	1.93947100	0.33622600
C	-7.45289700	-0.51357300	0.54981800
C	-7.12473600	-1.60214800	1.37761100
C	-6.40184800	0.26915200	0.02588800
C	-5.79637400	-1.89873300	1.67133100
H	-7.91419000	-2.20674000	1.81239200
C	-5.07632300	-0.02357200	0.31671200
H	-6.63021900	1.10038600	-0.63376900
C	-4.75163800	-1.11555100	1.14681900
H	-5.56483800	-2.73971600	2.31949800
H	-4.27798100	0.58122100	-0.09991900
C	-11.08043500	2.86805300	-0.20814000
C	-11.99627900	3.28894900	-1.19444700
C	-10.59931800	3.82302600	0.70384600
C	-12.41373100	4.61293900	-1.26686900
H	-12.36478000	2.57406500	-1.92372300
C	-11.01790900	5.15105300	0.63191400
H	-9.91129400	3.52229400	1.48772600
C	-11.92919000	5.56574100	-0.35240900
H	-13.11187900	4.92489000	-2.03655200
H	-10.63942200	5.87160300	1.35248400
C	-12.10952500	-2.03294300	-0.53615200
C	-11.73515300	-3.18689500	-1.25522400
C	-13.42651600	-1.94860800	-0.05277500
C	-12.64188600	-4.21589200	-1.48215100
H	-10.72990400	-3.26507800	-1.65782700
C	-14.33635100	-2.98034100	-0.28006500
H	-13.73573000	-1.08236600	0.52361700
C	-13.95912300	-4.12736900	-0.99648100
H	-12.34260800	-5.09423400	-2.04430900
H	-15.34766700	-2.89818200	0.10988600

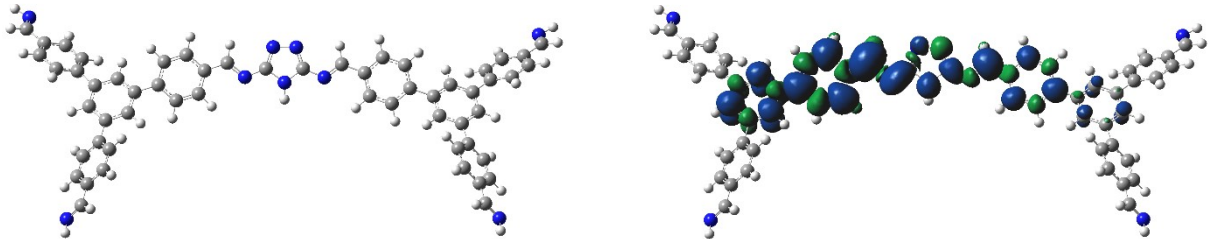
C	-3.37422600	-1.46154800	1.47761200
H	-3.23433800	-2.32358700	2.13869800
C	-12.34707400	6.97852600	-0.39816100
H	-11.89620600	7.61653600	0.37345000
C	-14.94916600	-5.19699900	-1.21637700
H	-15.93926900	-5.00264000	-0.78312200
N	-2.36365000	-0.79789300	1.02119200
N	-13.17138400	7.43753700	-1.26699800
N	-14.68603200	-6.27397200	-1.86132400
C	-1.09172600	-1.17190000	1.39703900
N	0.00000300	-0.59423300	0.81189600
N	-0.68654800	-2.04815400	2.31122900
C	1.09173600	-1.17190300	1.39704200
H	0.00000400	0.10500000	0.08076600
N	0.68655000	-2.04815400	2.31123400
N	2.36365400	-0.79789400	1.02117600
C	3.37422700	-1.46157700	1.47756400
H	3.23434400	-2.32363400	2.13862300
H	-15.51001200	-6.87685400	-1.89598200
C	4.75164100	-1.11557900	1.14675900
C	5.07632000	-0.02358700	0.31666800
C	5.79638100	-1.89877100	1.67124800
C	6.40184400	0.26914300	0.02584000
H	4.27797800	0.58121300	-0.09995000
C	7.12474000	-1.60217800	1.37752600
H	5.56485400	-2.73976800	2.31939900
C	7.45289800	-0.51358700	0.54975200
H	6.63020500	1.10038600	-0.63381000
H	7.91419400	-2.20677800	1.81229500
C	8.86806000	-0.19531800	0.23380400
C	9.30097900	1.13758300	0.16001200
C	9.79656900	-1.22225800	0.00365500
C	10.63581600	1.45249500	-0.13625400
H	8.59166200	1.93946800	0.33611000
C	11.13702300	-0.93595000	-0.29606700
H	9.47166600	-2.25601800	0.05742500
C	11.54257600	0.40589400	-0.36318500
C	11.08039200	2.86807600	-0.20823100
C	12.10957200	-2.03291300	-0.53608900
H	12.57684000	0.63818600	-0.59471700
C	10.59922500	3.82306700	0.70371000
C	11.99626000	3.28896300	-1.19452000
C	11.73524300	-3.18689400	-1.25513600
C	13.42654900	-1.94853600	-0.05267800
C	11.01778700	5.15110200	0.63175100
H	9.91118600	3.52234400	1.48758100
C	12.41368300	4.61296100	-1.26697000
H	12.36480600	2.57406600	-1.92375900
C	12.64200200	-4.21588200	-1.48200400
H	10.73000800	-3.26510700	-1.65776500
C	14.33641100	-2.98025800	-0.27991300
H	13.73572900	-1.08227000	0.52369500
C	11.92908700	5.56578100	-0.35255700
H	10.63926200	5.87166400	1.35228800
H	13.11185300	4.92490300	-2.03663700
C	13.95922300	-4.12731700	-0.99629900

H	12.34275700	-5.09424700	-2.04414200
H	15.34771500	-2.89806500	0.11006000
C	12.34693200	6.97857700	-0.39834600
C	14.94929300	-5.19693700	-1.21612900
H	11.89606300	7.61659100	0.37326100
N	13.17119600	7.43759600	-1.26722200
H	15.93939700	-5.00251700	-0.78290500
N	14.68617700	-6.27396700	-1.86098800
H	15.51017500	-6.87682800	-1.89561500
H	-13.32155800	8.43722400	-1.11988000
H	13.32134300	8.43729100	-1.12013200

Sum of electronic and thermal Free Energies = -2650.963109 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 415.7 nm.

Table S8: DFT-optimized geometry of **[TFPB-TRZ-TFPB]$^{-}$ (*$^{-}$)** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)



Spin Density Distribution

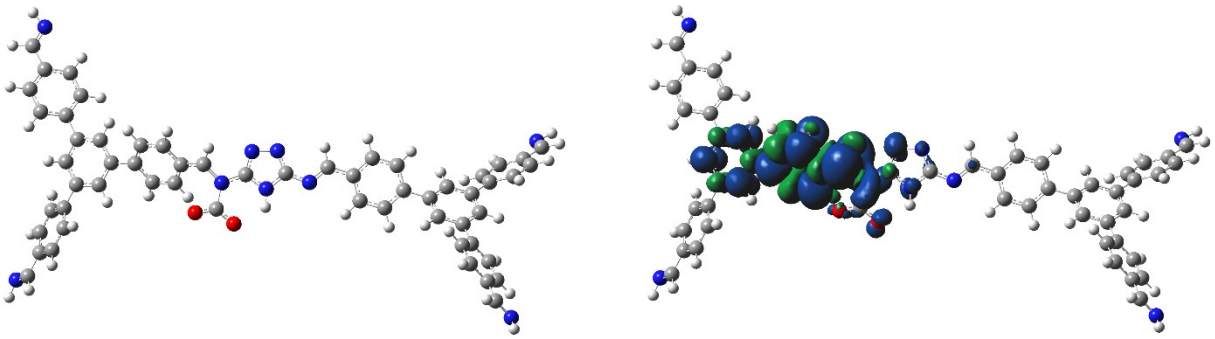
Atom	x	y	z
C	-8.89312300	-0.25756000	0.20136900
C	-9.87863800	-1.22267000	-0.06391600
C	-11.21736600	-0.85966200	-0.27448100
C	-11.56737600	0.49840200	-0.22064200
C	-10.60430800	1.48530700	0.04052000
C	-9.27345500	1.09369800	0.25002300
H	-9.59939800	-2.27018800	-0.10747300
H	-12.59962800	0.78987100	-0.38401100
H	-8.52365700	1.85070900	0.45455900
C	-7.48236700	-0.65633600	0.42623300
C	-7.16232400	-1.83762600	1.12284800
C	-6.41646200	0.13729600	-0.05101400
C	-5.83803200	-2.20857000	1.33479800
H	-7.95720500	-2.45888400	1.52404500
C	-5.09377500	-0.22960600	0.15682600
H	-6.63198900	1.04103900	-0.61316600
C	-4.77390100	-1.41421300	0.85791300

H	-5.61948400	-3.12036000	1.88497000
H	-4.28964500	0.38921700	-0.22712900
C	-10.98805600	2.91942800	0.09546900
C	-11.93115500	3.45034300	-0.80892500
C	-10.42201700	3.78371000	1.04848400
C	-12.29349500	4.79157000	-0.76260700
H	-12.36550700	2.80764700	-1.56853100
C	-10.78482900	5.12916100	1.09533300
H	-9.71064500	3.39795100	1.77192300
C	-11.72428200	5.65293600	0.19285400
H	-13.01389300	5.18829900	-1.47021800
H	-10.34030800	5.77773600	1.84594900
C	-12.24677700	-1.89470900	-0.55010700
C	-11.95736300	-3.00121500	-1.37527500
C	-13.53488700	-1.79800100	0.00394100
C	-12.91726800	-3.97235000	-1.63585900
H	-10.97661100	-3.08600800	-1.83310900
C	-14.49811100	-2.77174400	-0.25688500
H	-13.77889500	-0.96891400	0.66071500
C	-14.20502900	-3.87196300	-1.07854900
H	-12.68286300	-4.81340200	-2.27983300
H	-15.48528500	-2.68130800	0.18919200
C	-3.40464700	-1.83573900	1.10221400
H	-3.27358600	-2.77097900	1.65688000
C	-12.08319500	7.08011900	0.27301900
H	-11.56627700	7.64032100	1.06341100
C	-15.24892200	-4.88158400	-1.32993100
H	-16.20897200	-4.68253600	-0.83539700
N	-2.37887800	-1.14877500	0.69120400
N	-12.93121700	7.63488600	-0.51346500
N	-15.06233600	-5.91554900	-2.06583900
C	-1.10638900	-1.58385800	0.94154700
N	-0.01510000	-0.85308800	0.52811100
N	-0.67918700	-2.67967700	1.56336800
C	1.10676400	-1.55177800	0.92867100
H	-0.02997600	0.02647800	0.03317000
N	0.68986100	-2.67191600	1.56185700
N	2.34668500	-1.09671900	0.67289000
C	3.40648700	-1.79805900	1.10119600
H	3.26377100	-2.72652900	1.66189100
H	-15.91239400	-6.48075400	-2.10510200
C	4.74959500	-1.38800500	0.86091600
C	5.08813800	-0.20258100	0.13917100
C	5.84103600	-2.16872500	1.34538200
C	6.40778900	0.16232300	-0.06917200
H	4.28739400	0.41153800	-0.26001900
C	7.15685900	-1.79797700	1.12597200
H	5.63029200	-3.07373400	1.91152900
C	7.48960100	-0.61736600	0.41247100
H	6.61248300	1.05958900	-0.64719700
H	7.94843400	-2.41621200	1.54016500
C	8.89118200	-0.22189700	0.18051800
C	9.25704900	1.13423700	0.05799900
C	9.91458400	-1.18591800	0.07312700
C	10.58439900	1.52396500	-0.16817100
H	8.49359200	1.90005300	0.14252500

C	11.25112100	-0.82324600	-0.14477700
H	9.66401800	-2.23783800	0.15801800
C	11.57887400	0.53701300	-0.26759000
C	10.93541300	2.96220800	-0.29474900
C	12.30664000	-1.86399300	-0.24800600
H	12.60972700	0.82777500	-0.44007500
C	10.32542200	3.93144900	0.52080000
C	11.89149600	3.39377200	-1.23807700
C	12.06275700	-3.08049900	-0.91954200
C	13.57709300	-1.66445900	0.32014100
C	10.65684400	5.28002900	0.39712300
H	9.60288100	3.62658000	1.27127700
C	12.22294200	4.73812700	-1.36206500
H	12.36080700	2.66711100	-1.89417000
C	13.04689400	-4.05732600	-1.01722100
H	11.09742400	-3.24916600	-1.38684800
C	14.56507900	-2.64345400	0.22244800
H	13.78711200	-0.74717400	0.86125400
C	11.60901300	5.70402000	-0.54386800
H	10.17794300	6.01074200	1.04411900
H	12.95342200	5.05593800	-2.09881400
C	14.31616100	-3.85306000	-0.44583300
H	12.84707200	-4.98462700	-1.54396300
H	15.53738400	-2.47051900	0.67706500
C	11.93352400	7.13750300	-0.64506400
C	15.38413700	-4.86453500	-0.52817600
H	11.38121900	7.78376800	0.05008600
N	12.79168300	7.60631600	-1.47567200
H	16.32501400	-4.58025200	-0.03845800
N	15.23851400	-5.99240300	-1.12217200
H	16.09927800	-6.53899600	-1.06027500
H	-13.03051800	8.62571700	-0.28555300
H	12.86122100	8.62080600	-1.37830000

Sum of electronic and thermal Free Energies = -2651.075577 (Hartree/Particle).

Table S9: DFT-optimized geometry of ***CO_2^-** (doublet) (**model-b**), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)



Spin Density Distribution

Atom	x	y	z
C	8.86335300	-0.38494900	-0.10560100
C	9.55623100	-1.45194700	0.48714900
C	10.92554300	-1.35737200	0.77817300
C	11.60235300	-0.16823200	0.46650400
C	10.93464300	0.91479700	-0.12547800
C	9.56507800	0.79292200	-0.40549900
H	9.02328100	-2.36644300	0.72554400
H	12.66123700	-0.08479400	0.68808600
H	9.03949700	1.62472500	-0.86270000
C	7.41486600	-0.50030600	-0.41049900
C	6.87158800	-1.70415100	-0.89330300
C	6.54637500	0.59609900	-0.22368600
C	5.51259200	-1.80914100	-1.17953400
H	7.51974400	-2.55701600	-1.06806500
C	5.19085500	0.49451800	-0.50781600
H	6.93786900	1.52874400	0.17052600
C	4.65023000	-0.71326400	-0.99312300
H	5.11557300	-2.74638300	-1.56048200
H	4.53350100	1.34293700	-0.34998300
C	11.66393600	2.16795400	-0.44873700
C	12.64415700	2.67981300	0.42652300
C	11.39509500	2.87562000	-1.63290300
C	13.32769500	3.85338800	0.13011100
H	12.85336900	2.16296000	1.35807600
C	12.08052600	4.05268000	-1.93089200
H	10.66181300	2.49305000	-2.33587400
C	13.05507100	4.55882600	-1.05600500
H	14.07267900	4.24079500	0.81715300
H	11.86224200	4.57969600	-2.85626000
C	11.64581400	-2.49535400	1.40503500
C	11.03636900	-3.26799000	2.41521200
C	12.95188600	-2.83015200	1.00835600
C	11.70657100	-4.33296200	3.00603800
H	10.03650700	-3.01457500	2.75401100
C	13.62444800	-3.89852100	1.60026100
H	13.43693000	-2.26695400	0.21724500
C	13.01367400	-4.66479300	2.60581000
H	11.22938200	-4.91312700	3.78889100
H	14.63094400	-4.14549500	1.27210000
C	3.23273800	-0.86513700	-1.30842800
H	2.91880500	-1.85002000	-1.67143200
C	13.75747700	5.80706700	-1.40382200
H	13.45071000	6.25667800	-2.35741100
C	13.75588200	-5.78668100	3.20829300
H	14.76698500	-5.93697900	2.80742800
N	2.38568700	0.09995800	-1.17280500
N	14.65727700	6.33607800	-0.65836100
N	13.26875700	-6.53495200	4.12912700
C	1.05637500	-0.11679600	-1.47314800
N	0.16402600	0.92566700	-1.42177400
N	0.42176100	-1.22692000	-1.80965500

C	-1.04498500	0.39054500	-1.73810900
H	0.27782200	1.89678100	-1.14317200
N	-0.91631100	-0.91531300	-1.97342000
N	-2.23229500	1.09726300	-1.81951800
C	-3.30601400	0.41843500	-2.42196100
H	-3.05971600	-0.16610900	-3.30361300
H	13.94763400	-7.24753800	4.40289600
C	-4.61375700	0.36933500	-1.89349200
C	-4.97031000	0.89865200	-0.61891500
C	-5.64718600	-0.27014000	-2.64024100
C	-6.26616900	0.79936400	-0.14092000
H	-4.20889000	1.36988600	-0.00807700
C	-6.93971900	-0.36307100	-2.15090500
H	-5.41369400	-0.68083100	-3.61916400
C	-7.28896700	0.17214000	-0.88986100
H	-6.49101800	1.18927200	0.84753700
H	-7.70178100	-0.83533500	-2.76380700
C	-8.67145400	0.07520100	-0.36928900
C	-9.22279900	1.10968700	0.40669700
C	-9.46641400	-1.05286700	-0.63754600
C	-10.53078000	1.03176700	0.90756700
H	-8.62502900	1.98894300	0.62234200
C	-10.77845600	-1.15575600	-0.15215800
H	-9.05668500	-1.86326800	-1.23110800
C	-11.29993100	-0.10673100	0.62098900
C	-11.09417000	2.13712600	1.72488100
C	-11.60248600	-2.35579200	-0.44904900
H	-12.31298800	-0.17736700	1.00294100
C	-10.82365900	3.48000800	1.40994200
C	-11.91606600	1.86663600	2.83874200
C	-11.03055400	-3.64504900	-0.44806000
C	-12.97321900	-2.23774900	-0.73698300
C	-11.35452100	4.51398200	2.18003400
H	-10.21280900	3.71885100	0.54507200
C	-12.44585900	2.89695600	3.60695500
H	-12.12130700	0.83701600	3.11532300
C	-11.79828400	-4.77091800	-0.72283600
H	-9.97864700	-3.76393800	-0.20715200
C	-13.74392700	-3.36645200	-1.01270000
H	-13.43536600	-1.25602600	-0.76724100
C	-12.17232600	4.23951100	3.28792800
H	-11.13845400	5.54542700	1.91316900
H	-13.06935300	2.67328600	4.46626200
C	-13.17001600	-4.64791600	-1.00969500
H	-11.34674300	-5.75738800	-0.70965000
H	-14.80055200	-3.25057600	-1.24043100
C	-12.71528900	5.35907100	4.07757500
C	-14.01670800	-5.81756300	-1.30437300
H	-12.42505800	6.35617900	3.72070400
N	-13.46858700	5.19442200	5.10278300
H	-15.06858700	-5.58232300	-1.51425200
N	-13.57158500	-7.02056800	-1.31694500
H	-14.32356200	-7.67414500	-1.54266800
H	15.01159800	7.19383700	-1.08529700
H	-13.73056500	6.09887200	5.49889400
C	-2.28557400	2.56685300	-1.56442000

O	-3.31839700	3.13439200	-1.96143600
O	-1.27902100	3.04836200	-0.98170300

Sum of electronic and thermal Free Energies = -2839.673715 (Hartree/Particle).

Table S10: DFT-optimized geometry of **model-a** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.85545400	-0.10897200	0.10204000
C	-9.68789300	-1.23090100	-0.03308600
C	-11.01939700	-1.10022700	-0.45533800
C	-11.51430500	0.18093500	-0.74355100
C	-10.70439700	1.31984200	-0.61667700
C	-9.37609000	1.16028100	-0.19412400
H	-9.29489300	-2.21687200	0.19155600
H	-12.54285500	0.29275900	-1.07041000
H	-8.74146400	2.03437900	-0.09312200
C	-7.44911800	-0.26167900	0.55087400
C	-7.10583400	-1.19538700	1.54586200
C	-6.42210300	0.52790200	-0.01040600
C	-5.78648900	-1.33562900	1.96551700
H	-7.87927600	-1.79840800	2.01031000
C	-5.10536700	0.39154700	0.40534200
H	-6.66047700	1.23812300	-0.79574300
C	-4.76559900	-0.54512200	1.40375100
H	-5.54293700	-2.05579900	2.74186200
H	-4.32455600	0.99867300	-0.03985000
C	-11.24300900	2.66951900	-0.92477400
C	-12.11117600	2.86870400	-2.01812100
C	-10.90073200	3.78099100	-0.13571300
C	-12.61658200	4.13001700	-2.31151700
H	-12.37206300	2.02940300	-2.65554900
C	-11.40769800	5.04623100	-0.42934700
H	-10.25241900	3.65287700	0.72543000
C	-12.27144400	5.23986900	-1.51913800
H	-13.27628400	4.27090500	-3.16126800
H	-11.13658700	5.89083700	0.19896700
C	-11.89013200	-2.29597100	-0.59195000
C	-11.38309100	-3.50369300	-1.11442600
C	-13.23997000	-2.25378800	-0.20311900
C	-12.19388400	-4.62563000	-1.24249100
H	-10.34942900	-3.55352100	-1.44277600
C	-14.05350800	-3.37885200	-0.33095900
H	-13.65084700	-1.34395900	0.22306400
C	-13.54413100	-4.57955200	-0.85061400
H	-11.79320800	-5.54600200	-1.65425800
H	-15.09253400	-3.32706300	-0.01574700
C	-3.40057500	-0.72135400	1.87215900
H	-3.24504000	-1.46916200	2.65662800

C	-12.78655900	6.59224900	-1.79899200
H	-12.44134600	7.36868900	-1.10360900
C	-14.43430900	-5.74847500	-0.96821600
H	-15.46364400	-5.57872100	-0.62558600
N	-2.40834600	-0.03774000	1.39320600
N	-13.57609600	6.85291200	-2.77558900
N	-14.04746600	-6.87989100	-1.43214800
C	-1.15790900	-0.22817300	1.91769400
N	-0.05813700	0.29586000	1.32544200
N	-0.79446800	-0.88277500	3.03908700
C	1.02811400	-0.06189300	2.11176000
H	-0.03070400	0.84051600	0.47411200
N	0.54207000	-0.79050900	3.16709800
N	2.26047700	0.28069000	1.81134500
C	3.29560100	-0.10867300	2.73640500
H	3.10142900	-1.09271100	3.17696900
H	-14.81969900	-7.54863100	-1.42546700
C	4.64888400	-0.11981400	2.05266000
C	5.01555700	0.88580800	1.14634100
C	5.58724900	-1.11639100	2.35056300
C	6.28074400	0.89474800	0.55962000
H	4.29673400	1.65795900	0.89191700
C	6.85451100	-1.10983900	1.76553300
H	5.32815500	-1.90233300	3.05472400
C	7.22680300	-0.10303300	0.85797600
H	6.52823700	1.67381500	-0.15575300
H	7.56587000	-1.88646600	2.03115200
C	8.57426200	-0.09581200	0.23069200
C	9.26353700	1.10966100	0.02582000
C	9.18591700	-1.29444600	-0.16864400
C	10.53600500	1.13172800	-0.56592200
H	8.80186500	2.04352800	0.32948900
C	10.46000000	-1.30331600	-0.75713000
H	8.66368800	-2.23329500	-0.01612600
C	11.12392500	-0.08254000	-0.95204000
C	11.24946500	2.41736700	-0.77798900
C	11.09525400	-2.58243100	-1.16600900
H	12.10828200	-0.07799000	-1.40845500
C	11.19660700	3.44149700	0.18331400
C	11.99872500	2.64304700	-1.95145100
C	10.33332400	-3.61396800	-1.75317800
C	12.47143300	-2.79798900	-0.97772300
C	11.86802000	4.64634600	-0.02090000
H	10.64585300	3.28766400	1.10595900
C	12.66829900	3.84397100	-2.15575900
H	12.03602200	1.87592800	-2.71882300
C	10.92333000	-4.81305000	-2.13606000
H	9.27279600	-3.46245200	-1.92933100
C	13.06381600	-4.00050900	-1.36108200
H	13.07839600	-2.03037500	-0.50797900
C	12.61295000	4.86601900	-1.19071500
H	11.82011600	5.42154800	0.73969700
H	13.23320700	4.00634800	-3.06763100
C	12.30077800	-5.02480100	-1.94413700
H	10.32665600	-5.59462100	-2.59471800
H	14.12819500	-4.14925700	-1.19785400

C	13.30869700	6.15265500	-1.37063300
C	12.96185900	-6.28287100	-2.33383900
H	13.18256300	6.86246900	-0.54239900
N	14.00885300	6.43293500	-2.40835800
H	14.04016700	-6.31793800	-2.12923000
N	12.33715900	-7.26656000	-2.87009400
H	12.98269200	-8.03539000	-3.05927600
H	-13.80889200	7.84753100	-2.78730400
H	14.40016600	7.37315700	-2.32827000
C	3.37974100	0.88344600	4.00184700
O	2.81450800	1.99839900	3.90513000
O	4.03672300	0.41682800	4.96546500

Sum of electronic and thermal Free Energies = -2839.658638 (Hartree/Particle).

Table S11: DFT-optimized geometry of **model-c** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.76847200	-0.32782500	0.07959700
C	-9.81354800	-1.27016900	-0.01293800
C	-11.14544000	-0.87965800	-0.20987200
C	-11.44688000	0.48708500	-0.32764900
C	-10.43056900	1.45294900	-0.24327800
C	-9.10843400	1.03579200	-0.03671200
H	-9.58406300	-2.32723000	0.06731100
H	-12.47394500	0.79928100	-0.48454300
H	-8.32844600	1.78592200	0.03678700
C	-7.37217900	-0.75219400	0.28980600
C	-7.05253900	-1.94616500	0.98772700
C	-6.28152500	0.01038700	-0.19999600
C	-5.74169400	-2.34453300	1.18617500
H	-7.85019500	-2.55314000	1.40684700
C	-4.96717500	-0.38177100	-0.01208000
H	-6.47576400	0.91593900	-0.76858400
C	-4.64136900	-1.57947400	0.69607000
H	-5.54097400	-3.25831500	1.74178700
H	-4.16079400	0.21789500	-0.42142400
C	-10.75360100	2.89805100	-0.36602700
C	-11.71273200	3.34840000	-1.29739400
C	-10.11346800	3.85516600	0.44065400
C	-12.01838400	4.69910400	-1.41824400
H	-12.20501000	2.63099500	-1.94680500
C	-10.41914900	5.21014100	0.32021700
H	-9.38755100	3.53600800	1.18188000
C	-11.37477700	5.65280200	-0.60861300
H	-12.75140700	5.03124400	-2.14604100
H	-9.91730600	5.93136800	0.96044700
C	-12.22403300	-1.89804800	-0.29620200
C	-12.01729100	-3.11840900	-0.97316000

C	-13.48012100	-1.67268300	0.29383400
C	-13.02346700	-4.07398300	-1.05541500
H	-11.06377800	-3.30662800	-1.45698100
C	-14.49014800	-2.63038100	0.21170400
H	-13.66143300	-0.75199100	0.83954200
C	-14.27828000	-3.84382300	-0.46235500
H	-12.85243500	-5.00446100	-1.58670500
H	-15.45071500	-2.43773200	0.68304900
C	-3.30327300	-2.01018200	0.91620800
H	-3.16206000	-2.95245800	1.45314700
C	-11.67232400	7.09237200	-0.70626000
H	-11.09642500	7.72807700	-0.02058700
C	-15.36874300	-4.83222400	-0.52832700
H	-16.29556200	-4.52838600	-0.02374100
N	-2.24280100	-1.29909500	0.50105100
N	-12.53435800	7.57742900	-1.52344900
N	-15.25653900	-5.96232900	-1.12530000
C	-1.00141500	-1.77188600	0.71345400
N	0.11412900	-1.03418300	0.36908700
N	-0.57657300	-2.94113700	1.24377100
C	1.20993800	-1.78567400	0.72550500
H	0.11497100	-0.09794000	-0.00923100
N	0.79511600	-2.93582200	1.24594700
N	2.48025800	-1.31915500	0.50976400
C	3.50773200	-1.98756700	0.93913800
H	3.38255200	-2.92357700	1.49401000
H	-16.12772900	-6.49043500	-1.05037700
C	4.87566000	-1.54379900	0.71730400
C	5.18722600	-0.36398100	0.00624600
C	5.94212600	-2.31146300	1.22862900
C	6.50711100	0.02527300	-0.17822500
H	4.38000900	0.23308200	-0.40466000
C	7.26396000	-1.91804500	1.04080000
H	5.72827500	-3.21943800	1.78678100
C	7.57627200	-0.74117700	0.33419500
H	6.71825200	0.92441100	-0.74918600
H	8.06139600	-2.51805300	1.46823200
C	8.98425700	-0.31864800	0.13380200
C	9.33756500	1.04006000	0.17154400
C	9.99265500	-1.26856800	-0.09691000
C	10.66501500	1.45403600	-0.01547000
H	8.56945600	1.78535600	0.34929700
C	11.32863900	-0.88309800	-0.28384000
H	9.73403100	-2.32167000	-0.13156500
C	11.65165800	0.48199300	-0.24185400
C	11.02062400	2.89583600	0.02597100
C	12.38309900	-1.90217600	-0.52166600
H	12.68157800	0.79083200	-0.38721600
C	10.41955900	3.76301600	0.95454500
C	11.97162500	3.43113500	-0.86745900
C	12.13321200	-3.02512000	-1.33746300
C	13.65590400	-1.77362800	0.06048900
C	10.75697100	5.11545500	0.98890200
H	9.70069000	3.37465600	1.66914000
C	12.30849300	4.77935000	-0.83368800
H	12.43264700	2.78579000	-1.60887500

C	13.11659800	-3.98170800	-1.56199000
H	11.16502100	-3.13450000	-1.81635800
C	14.64255600	-2.73284700	-0.16397900
H	13.86923300	-0.93111900	0.71081000
C	11.70497700	5.64348300	0.09791000
H	10.28569800	5.76641300	1.72090000
H	13.03535500	5.17907500	-1.53292000
C	14.38879900	-3.84960900	-0.97631700
H	12.91291200	-4.83591500	-2.19911300
H	15.61727100	-2.61805600	0.30341000
C	12.03704600	7.07783800	0.16530400
C	15.45663600	-4.84304200	-1.18841100
H	11.49365300	7.63952100	0.93664700
N	12.89200100	7.63670600	-0.61067400
H	16.40029400	-4.61960000	-0.67324300
N	15.30710700	-5.88991600	-1.91439900
H	16.16807500	-6.43970700	-1.92509600
H	-12.58225200	8.59316700	-1.42608500
H	12.96901200	8.63219900	-0.39473600
C	-2.15490500	1.37493500	1.50118200
O	-2.86752000	1.11715000	2.39076900
O	-1.43257800	1.70722900	0.64082500

Sum of electronic and thermal Free Energies = -2839.669197 (Hartree/Particle).

Table S12: DFT-optimized geometry of **model-d** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.85190000	-0.15401700	0.03810300
C	-9.67667000	-1.18314200	-0.44180800
C	-11.00966700	-0.93681900	-0.80366000
C	-11.51406200	0.36665200	-0.67776400
C	-10.71201100	1.41459000	-0.20057800
C	-9.38203500	1.14033900	0.15252100
H	-9.27629100	-2.18706900	-0.53587700
H	-12.54359700	0.56772200	-0.95488200
H	-8.75311000	1.94368900	0.52144900
C	-7.44353600	-0.42975000	0.41826300
C	-7.09277600	-1.62422800	1.07274400
C	-6.42243500	0.50163500	0.13231000
C	-5.77105100	-1.87993300	1.42796100
H	-7.86143500	-2.34723500	1.32588400
C	-5.10396800	0.25140200	0.48782300
H	-6.66621800	1.41990600	-0.39251100
C	-4.75714000	-0.94741500	1.14251400
H	-5.52166000	-2.80496400	1.94073300
H	-4.32793600	0.97317600	0.25636700
C	-11.26049200	2.78916700	-0.07237400
C	-12.13510300	3.31199700	-1.04736500

C	-10.92167700	3.60300800	1.02223800
C	-12.65001700	4.59810900	-0.93277900
H	-12.39383200	2.71057500	-1.91345500
C	-11.43796800	4.89304900	1.13771100
H	-10.26881900	3.21854600	1.79956800
C	-12.30815300	5.40938000	0.16436300
H	-13.31479400	4.99110000	-1.69483000
H	-11.16896200	5.50247100	1.99670800
C	-11.87138200	-2.03608200	-1.30942500
C	-11.35390600	-3.01852300	-2.17882200
C	-13.22293400	-2.12506100	-0.93443200
C	-12.15612400	-4.04940500	-2.65435100
H	-10.31873100	-2.95824700	-2.50058100
C	-14.02790000	-3.15905200	-1.41077700
H	-13.64220600	-1.39550700	-0.24872700
C	-13.50822000	-4.13518800	-2.27586100
H	-11.74702200	-4.79357300	-3.32953700
H	-15.06849700	-3.21380900	-1.10127300
C	-3.38636300	-1.25412400	1.53373600
H	-3.22822400	-2.21040800	2.04506000
C	-12.83377600	6.77760800	0.32006100
H	-12.49033200	7.30231200	1.22138300
C	-14.38996300	-5.21353700	-2.75785100
H	-15.42126700	-5.16541000	-2.38392000
N	-2.39817900	-0.45682700	1.29688700
N	-13.63035900	7.32228600	-0.52487800
N	-13.99449100	-6.14040000	-3.55137600
C	-1.14897000	-0.79616400	1.77275000
N	-0.01951900	-0.29287100	1.17823000
N	-0.85129700	-1.53057300	2.81434800
C	1.09025100	-0.78464700	1.84385900
H	0.02080800	0.21278100	0.30445800
N	0.53838400	-1.52755900	2.88581300
N	2.30250300	-0.56890900	1.40197600
C	3.38575300	-1.26921000	1.81083400
H	3.27760100	-2.11857200	2.48240400
H	-14.76241400	-6.78172200	-3.75784900
C	4.69677200	-0.94396000	1.36472200
C	4.97759000	0.16226900	0.50931700
C	5.80901800	-1.73704000	1.77220900
C	6.27121900	0.44218100	0.09825800
H	4.15480000	0.78354800	0.17132900
C	7.09747100	-1.44995700	1.35174900
H	5.63928800	-2.58082500	2.43711600
C	7.37151600	-0.35108600	0.50198600
H	6.43545900	1.27967100	-0.57432000
H	7.91551900	-2.06923000	1.70866400
C	8.74727400	-0.04561400	0.05470100
C	9.15979900	1.28146100	-0.16805000
C	9.68446000	-1.07300500	-0.16260700
C	10.45962700	1.58510300	-0.59826100
H	8.45715200	2.09124100	-0.00243700
C	10.99302800	-0.79735000	-0.58538700
H	9.38909800	-2.10426200	-0.00093600
C	11.37068100	0.53703200	-0.80378900
C	10.86819900	2.99497100	-0.82813900

C	11.96465000	-1.90060100	-0.80069200
H	12.37942100	0.76087100	-1.13465000
C	10.44456500	4.02112000	0.03413700
C	11.69277400	3.34031700	-1.91920600
C	11.56009800	-3.11911500	-1.38488000
C	13.31248800	-1.75950100	-0.42714700
C	10.82985900	5.34280200	-0.18645800
H	9.82817200	3.78176500	0.89494800
C	12.07736100	4.65784300	-2.14000300
H	12.01493800	2.56846200	-2.61147100
C	12.46542400	-4.15471600	-1.58572800
H	10.52952600	-3.24397000	-1.70274900
C	14.22121400	-2.79766100	-0.62816400
H	13.64785900	-0.84106300	0.04432300
C	11.65070100	5.68136100	-1.27423200
H	10.49718700	6.11888600	0.49823100
H	12.70414300	4.90980300	-2.98906500
C	13.81293300	-4.00924700	-1.20861800
H	12.14130200	-5.08330000	-2.04382300
H	15.25678400	-2.66965400	-0.32327400
C	12.03723500	7.08913600	-1.47437400
C	14.80196000	-5.08405800	-1.40306300
H	11.63232000	7.78709200	-0.72952200
N	12.78717100	7.48093800	-2.43870000
H	15.81739500	-4.84068400	-1.06293800
N	14.51198600	-6.21880000	-1.92663000
H	15.34188100	-6.81319200	-1.96648000
H	-13.87032000	8.26932000	-0.22636200
H	12.92801100	8.49156000	-2.38984700
C	1.16167700	-1.90084400	4.20364300
O	2.18797600	-1.25269800	4.48283600
O	0.55217600	-2.79326000	4.81988900

Sum of electronic and thermal Free Energies = -2839.666250 (Hartree/Particle).

Table S13: DFT-optimized geometry of **TS** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

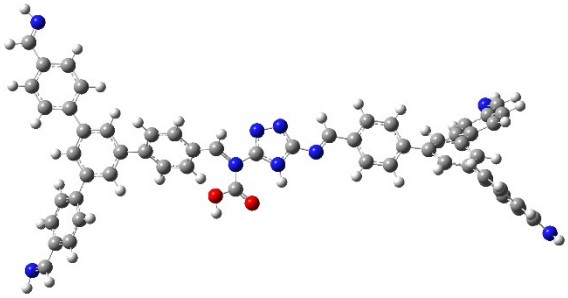
Atom	x	y	z
C	9.02010400	-0.36578300	-0.15927000
C	9.92479900	-1.31875600	0.33428900
C	11.27383900	-0.99836900	0.54966000
C	11.71360400	0.30309200	0.26266000
C	10.83162400	1.27574100	-0.23250600
C	9.48790200	0.92786300	-0.43805200
H	9.57386200	-2.32146900	0.55465600
H	12.75439400	0.56187500	0.42680700
H	8.79798600	1.67308700	-0.81990200
C	7.59518100	-0.71852900	-0.38076300
C	7.23118200	-1.97756300	-0.89095300

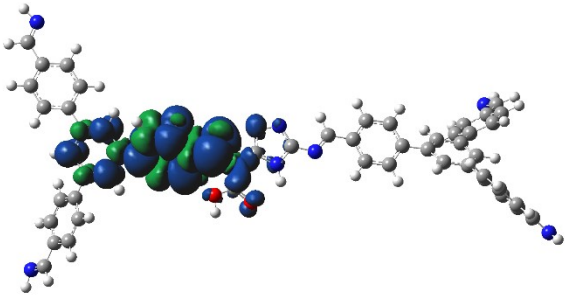
C	6.56738500	0.20159100	-0.08350100
C	5.89306200	-2.30495600	-1.09665700
H	8.00096800	-2.69760200	-1.15046700
C	5.23231300	-0.12203500	-0.28669600
H	6.82073600	1.17152700	0.33337000
C	4.87041700	-1.38479900	-0.79912600
H	5.63581100	-3.28072400	-1.50039000
H	4.45329800	0.59276000	-0.04366300
C	11.31154600	2.64887300	-0.53413700
C	12.24545600	3.28956600	0.30629900
C	10.84683700	3.34440600	-1.66356400
C	12.69610300	4.57508100	0.02902100
H	12.60206200	2.78115000	1.19684400
C	11.29867800	4.63360300	-1.94235000
H	10.14498300	2.86739900	-2.34039000
C	12.22825500	5.26760200	-1.10257100
H	13.40737700	5.05950100	0.68977000
H	10.93219500	5.15004900	-2.82584300
C	12.21944700	-2.01797500	1.07226500
C	11.81808700	-2.93439100	2.06634700
C	13.53745200	-2.09526400	0.59017000
C	12.69949000	-3.88983700	2.55893100
H	10.81199900	-2.88019900	2.47075900
C	14.42203800	-3.05320700	1.08399700
H	13.86725400	-1.41765600	-0.19104600
C	14.01780400	-3.96331900	2.07369900
H	12.37984000	-4.58328200	3.32973500
H	15.43449400	-3.10024700	0.69107700
C	3.48057400	-1.76691900	-1.02917500
H	3.31226300	-2.77327300	-1.42813200
C	12.68193700	6.63125800	-1.42983900
H	12.23707400	7.05808200	-2.33855900
C	14.98101800	-4.96156600	2.57165200
H	15.97511500	-4.91257300	2.10780300
N	2.49389000	-0.97035600	-0.77932500
N	13.52909000	7.27823100	-0.71639600
N	14.69174400	-5.82421100	3.47571300
C	1.19919900	-1.38295600	-1.00610300
N	0.15308400	-0.52247700	-0.77717700
N	0.72948700	-2.54515200	-1.42803300
C	-0.99279800	-1.21286800	-1.09199600
H	0.20009700	0.43767900	-0.46419400
N	-0.64692500	-2.45452900	-1.48295100
N	-2.22988500	-0.67062100	-0.96042500
C	-3.28809600	-1.36528800	-1.45296400
H	-3.10848700	-2.18639200	-2.14869900
H	15.50028700	-6.41698900	3.67174900
C	-4.63145000	-1.06217300	-1.11329600
C	-4.98951300	-0.11467600	-0.10668600
C	-5.70918100	-1.72575300	-1.77345700
C	-6.31507500	0.15608000	0.18954100
H	-4.20321000	0.38240700	0.45159000
C	-7.03062300	-1.45221100	-1.46428900
H	-5.48230800	-2.45213100	-2.55071200
C	-7.38013400	-0.49649500	-0.47759900
H	-6.53676900	0.86552100	0.98224500

H	-7.81364200	-1.96405500	-2.01672000
C	-8.79035300	-0.19891000	-0.15478600
C	-9.18339600	1.08617400	0.26632900
C	-9.78626900	-1.18922800	-0.25887100
C	-10.51783300	1.38358600	0.57807300
H	-8.43679300	1.86865000	0.35018300
C	-11.12925500	-0.91737600	0.03935000
H	-9.50986900	-2.18902200	-0.57630300
C	-11.48623100	0.37376100	0.46013200
C	-10.90211900	2.74882900	1.02099600
C	-12.15941900	-1.98090100	-0.08496400
H	-12.52216000	0.59336800	0.69612200
C	-10.31904700	3.88900200	0.44104800
C	-11.86283400	2.93690400	2.03666700
C	-11.88161700	-3.30809200	0.30401400
C	-13.43819700	-1.69292300	-0.59294100
C	-10.68108300	5.16802800	0.86141500
H	-9.59373800	3.77606500	-0.35853700
C	-12.22492200	4.21184900	2.45627700
H	-12.31179600	2.07182600	2.51501200
C	-12.84216700	-4.30634600	0.18888800
H	-10.90889800	-3.55106200	0.72057400
C	-14.40233800	-2.69347000	-0.70874200
H	-13.67350500	-0.68503000	-0.92017400
C	-11.63766500	5.34962600	1.87321200
H	-10.22239500	6.03531400	0.39315300
H	-12.95908000	4.33985800	3.24499300
C	-14.12013200	-4.01318700	-0.32111400
H	-12.61653900	-5.32103200	0.50001600
H	-15.38180600	-2.44943300	-1.11241600
C	-11.99343800	6.71737800	2.28979700
C	-15.16398700	-5.04378700	-0.45967500
H	-11.46140600	7.51369500	1.75253200
N	-12.85457000	6.97142400	3.20618500
H	-16.11495600	-4.68187900	-0.87274500
N	-14.98764300	-6.27039300	-0.12772100
H	-15.83582200	-6.81110500	-0.30577300
H	13.70182400	8.20048000	-1.12038000
H	-12.94715100	7.98059700	3.33494100
C	-2.26321400	1.44782800	-1.26480100
O	-3.11549400	1.58688800	-2.08108700
O	-1.41815300	1.85360900	-0.52112500

Sum of electronic and thermal Free Energies = -2839.660725 (Hartree/Particle).

Table S14: DFT-optimized geometry of ***COOH** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)





Spin Density Distribution

Atom	x	y	z
C	8.64826700	-0.43084600	-0.13793700
C	9.20662400	-1.56970600	0.46278500
C	10.57129300	-1.62678700	0.78370200
C	11.38097400	-0.51828000	0.49216800
C	10.84941700	0.63329900	-0.10826400
C	9.48098100	0.66381900	-0.41690300
H	8.57152100	-2.42071700	0.68530000
H	12.43748500	-0.55211400	0.73670100
H	9.06002300	1.55009000	-0.87992300
C	7.20223100	-0.38425900	-0.47049200
C	6.53780100	-1.52009800	-0.96682600
C	6.45847700	0.80241000	-0.29569800
C	5.18108200	-1.47317200	-1.27666400
H	7.09020600	-2.43933100	-1.13307800
C	5.10581300	0.85297300	-0.60390900
H	6.94471500	1.68511600	0.10754600
C	4.44369500	-0.28784400	-1.10080000
H	4.68835000	-2.35963900	-1.66689400
H	4.54477100	1.76967800	-0.45688100
C	11.71830500	1.80010400	-0.40888600
C	12.73014800	2.19779900	0.48935500
C	11.55298400	2.53808600	-1.59352000
C	13.54325500	3.29137700	0.21489900
H	12.86284500	1.65687800	1.42132300
C	12.36845900	3.63488000	-1.86944400
H	10.79755600	2.24081900	-2.31409400
C	13.37347600	4.02812500	-0.97136100
H	14.31170900	3.59175500	0.91940200
H	12.22849900	4.18655500	-2.79556500
C	11.14777500	-2.83802500	1.42194700
C	10.43218500	-3.54272100	2.41191900
C	12.41987000	-3.31123300	1.05720300
C	10.96772000	-4.67534400	3.01413500
H	9.45704400	-3.18360800	2.72641100
C	12.95741100	-4.44747900	1.66067400
H	12.98367200	-2.80189300	0.28198900
C	12.24148900	-5.14548400	2.64630900
H	10.40984200	-5.20220200	3.78107100
H	13.93960000	-4.80100500	1.35732000
C	3.02477500	-0.28217300	-1.43707000

H	2.61272500	-1.22099700	-1.82270300
C	14.21421400	5.19462900	-1.29578000
H	13.97848200	5.67981000	-2.25221700
C	12.84288300	-6.34184000	3.26258400
H	13.84198600	-6.59946000	2.88685900
N	2.28240100	0.76507000	-1.29135400
N	15.15002600	5.61871200	-0.52799700
N	12.25465200	-7.03451900	4.16772800
C	0.95264700	0.69927000	-1.64809200
N	0.12791000	1.77026700	-1.39682500
N	0.26243800	-0.26245000	-2.23810600
C	-1.09372800	1.39032200	-1.85314200
H	0.34478200	2.63968800	-0.92511400
N	-1.04276500	0.17328200	-2.36478400
N	-2.25952400	2.16438900	-1.83034300
C	-3.36043500	1.66863400	-2.59392700
H	-3.14675200	1.48547900	-3.64037700
H	12.84556200	-7.81644600	4.45571400
C	-4.60188700	1.33569500	-2.02200900
C	-4.86192800	1.39226000	-0.62182100
C	-5.66604300	0.90530400	-2.86959800
C	-6.10393400	1.05121000	-0.11514000
H	-4.07044700	1.68436800	0.05987800
C	-6.90182800	0.56453100	-2.34841900
H	-5.50171200	0.85753400	-3.94239600
C	-7.15780900	0.63243200	-0.95945600
H	-6.25830600	1.07908000	0.95903000
H	-7.69506300	0.26434000	-3.02591900
C	-8.48320100	0.27246400	-0.40572200
C	-9.01651400	0.97251600	0.68950400
C	-9.23455000	-0.77600600	-0.96297800
C	-10.27018000	0.64277700	1.22530200
H	-8.44968500	1.78627300	1.12932400
C	-10.49044700	-1.12731600	-0.44638500
H	-8.83502200	-1.32775900	-1.80729400
C	-10.99698900	-0.41027400	0.64868300
C	-10.81832700	1.39599000	2.38258800
C	-11.27038400	-2.24000300	-1.04695100
H	-11.96719900	-0.67483300	1.05595900
C	-10.65523100	2.78855500	2.48017000
C	-11.51542200	0.73200300	3.41320100
C	-10.62981900	-3.41864400	-1.48222600
C	-12.66490000	-2.14717900	-1.19543400
C	-11.16956500	3.49171800	3.56874000
H	-10.14297400	3.32859500	1.69009500
C	-12.02765900	1.43239900	4.49933100
H	-11.63479900	-0.34626500	3.37088100
C	-11.35487800	-4.46334700	-2.04370900
H	-9.55639300	-3.52252300	-1.35687300
C	-13.39265000	-3.19443300	-1.75920900
H	-13.18144100	-1.24286100	-0.88927100
C	-11.86170200	2.82612900	4.59309600
H	-11.03932800	4.56970000	3.61982300
H	-12.55339100	0.90742600	5.29006900
C	-12.75043300	-4.36576000	-2.19134600
H	-10.85065400	-5.36850800	-2.36563200

H	-14.46953100	-3.09839000	-1.87256900
C	-12.38883100	3.60329700	5.72912100
C	-13.55291000	-5.45139900	-2.78265900
H	-12.19438000	4.68277000	5.67712600
N	-13.02495800	3.07100800	6.70749900
H	-14.63016300	-5.24723900	-2.84152800
N	-13.04328800	-6.55222000	-3.19914500
H	-13.77340200	-7.16318900	-3.56964700
H	15.60498000	6.43472900	-0.94100800
H	-13.29868400	3.78625600	7.38362000
C	-2.26083300	3.41196600	-1.22298300
O	-1.32338200	3.86844600	-0.57983500
O	-3.41497800	4.06470700	-1.42683000
H	-3.35579700	4.91811900	-0.96580800

Sum of electronic and thermal Free Energies = -2840.110258 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 473.08 nm.

Table S15: DFT-optimized geometry of ***COOH**$^-$ (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

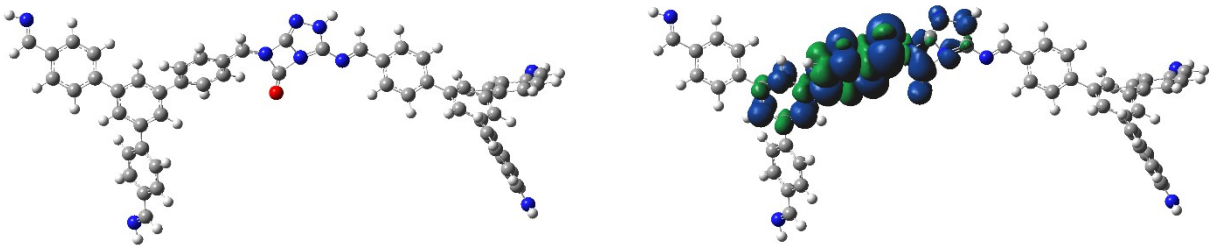
Atom	x	y	z
C	-7.91440800	0.26193200	-0.53606500
C	-8.28066700	1.59723100	-0.76550300
C	-9.60077900	2.03199500	-0.57315200
C	-10.56225700	1.10439700	-0.14361300
C	-10.22414900	-0.23680900	0.09317200
C	-8.89628100	-0.64400000	-0.10620800
H	-7.52936500	2.30638000	-1.09687200
H	-11.58584100	1.43068400	0.00839100
H	-8.62438100	-1.67859500	0.07462700
C	-6.51383400	-0.18462200	-0.74414600
C	-5.75104400	0.30469900	-1.81940900
C	-5.91315500	-1.11285900	0.13275800
C	-4.43784900	-0.11728700	-2.01224200
H	-6.19472300	1.00211200	-2.52277300
C	-4.60420900	-1.53566500	-0.05679700
H	-6.47425000	-1.48710800	0.98333600
C	-3.84311000	-1.04351400	-1.13610700
H	-3.86919500	0.26657400	-2.85502300
H	-4.15295700	-2.24337300	0.63041100
C	-11.25260700	-1.20790700	0.54701200
C	-12.24065600	-0.83118200	1.48016300
C	-11.26660100	-2.52595500	0.05925000
C	-13.20423900	-1.73671400	1.90897200
H	-12.23671700	0.17477400	1.88850900
C	-12.23284200	-3.43465600	0.48902400
H	-10.53195400	-2.83721800	-0.67673300

C	-13.21436600	-3.05502400	1.41835400
H	-13.95342100	-1.43629100	2.63398000
H	-12.22972400	-4.44691400	0.09284900
C	-9.97397900	3.44845400	-0.82037800
C	-9.10904500	4.49900800	-0.45014000
C	-11.19743700	3.77728800	-1.42884300
C	-9.45396700	5.82604900	-0.67911600
H	-8.16842700	4.27089300	0.04175100
C	-11.54380200	5.10812200	-1.65902300
H	-11.87253200	2.98824200	-1.74497100
C	-10.67936800	6.15072300	-1.28887000
H	-8.78282400	6.62478700	-0.38130600
H	-12.49146000	5.33951400	-2.13869900
C	-2.46472100	-1.46062200	-1.37480400
H	-1.96665400	-1.01924700	-2.24512900
C	-14.21920500	-4.04302000	1.85032300
H	-14.11747600	-5.03442500	1.38936200
C	-11.07939500	7.54534000	-1.54885100
H	-12.05764700	7.66018200	-2.03419100
N	-1.85364000	-2.30280600	-0.61003200
N	-15.14401400	-3.77627000	2.69809700
N	-10.34993300	8.55315000	-1.23694200
C	-0.55849200	-2.67097700	-0.91131800
N	0.15107400	-3.45389400	-0.03498900
N	0.18635900	-2.41300800	-1.97237600
C	1.36705700	-3.64825800	-0.61861300
H	-0.12718200	-3.82484200	0.86565700
N	1.41000200	-3.03072200	-1.79154500
N	2.42258500	-4.39279300	-0.07838800
C	3.66269200	-4.46008700	-0.81425500
H	3.72580800	-5.24396600	-1.55924100
H	-10.81392000	9.42308000	-1.50432600
C	4.66140600	-3.52237500	-0.59638800
C	4.55854100	-2.44383200	0.35811600
C	5.90915100	-3.56147400	-1.32356300
C	5.58542300	-1.53793000	0.55671400
H	3.64015200	-2.33142200	0.92885400
C	6.91417200	-2.63899400	-1.11438900
H	6.06106300	-4.35691800	-2.05106100
C	6.80723000	-1.58574500	-0.16291600
H	5.42144700	-0.73897300	1.27654200
H	7.83361500	-2.75253100	-1.68436800
C	7.88589400	-0.61614400	0.05795800
C	8.01740700	0.08245700	1.28142000
C	8.84757600	-0.33261200	-0.94052200
C	9.03808700	1.01618100	1.50332400
H	7.30700600	-0.10811800	2.07853100
C	9.88595800	0.58633600	-0.73849300
H	8.78289400	-0.83982100	-1.89707400
C	9.97715000	1.26570200	0.48816000
C	9.13366700	1.72928900	2.80378100
C	10.87754800	0.84844500	-1.81411900
H	10.77391200	1.98336900	0.65160800
C	8.86855600	1.06845200	4.01647700
C	9.49542200	3.09218100	2.85775100
C	10.48217400	0.91671700	-3.16699100

C	12.23795900	1.03993600	-1.51362700
C	8.95914800	1.74272500	5.23343400
H	8.61027300	0.01420700	4.00893200
C	9.58676000	3.76569900	4.07038500
H	9.68534200	3.63064400	1.93430100
C	11.40614200	1.16513000	-4.17540800
H	9.43437100	0.79444600	-3.42353800
C	13.16579300	1.28964400	-2.52392700
H	12.57550800	0.97255100	-0.48414400
C	9.31954800	3.09926300	5.28039600
H	8.75707400	1.20808800	6.15835000
H	9.85719900	4.81632000	4.09334000
C	12.76583800	1.35652100	-3.86842700
H	11.08446000	1.22288200	-5.21011600
H	14.21345200	1.42672400	-2.26747500
C	9.40611500	3.77696100	6.58513400
C	13.77425700	1.62467300	-4.90773400
H	9.16895200	3.14161700	7.44890800
N	9.73164800	5.01128500	6.71682600
H	14.79903600	1.74655400	-4.53210500
N	13.49165800	1.71229300	-6.15644400
H	14.33662800	1.90252400	-6.69810900
H	-15.72883000	-4.59893000	2.85539400
H	9.72869300	5.27465100	7.70379500
C	2.25257300	-5.01388100	1.13862800
O	1.23193100	-4.96562100	1.83180600
O	3.33953300	-5.71054700	1.52703100
H	3.12004700	-6.10086500	2.38920000

Sum of electronic and thermal Free Energies = -2840.234404 (Hartree/Particle).

Table S16: DFT-optimized geometry of ***CO**$^{+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)



Spin Density Distribution

Atom	x	y	z
C	8.28094300	-0.57376700	0.09697800
C	9.02336700	-0.54969800	1.28823000
C	10.29227600	0.04538900	1.33810400

C	10.81707000	0.61447200	0.16745600
C	10.09842400	0.60020300	-1.03793600
C	8.82794600	0.00660600	-1.05830500
H	8.60801600	-0.99271200	2.18700600
H	11.79879100	1.07551200	0.19546300
H	8.26282600	-0.00727700	-1.98404300
C	6.93957300	-1.20180600	0.06020900
C	6.67044300	-2.37044300	0.80052000
C	5.90116600	-0.63784600	-0.71685100
C	5.41230800	-2.95562200	0.76872900
H	7.45884700	-2.83382300	1.38346200
C	4.64408200	-1.21579700	-0.75401300
H	6.08271200	0.27578800	-1.27249900
C	4.37992100	-2.38868500	-0.00976800
H	5.22394300	-3.86168700	1.33732800
H	3.85106400	-0.76825000	-1.34313900
C	10.67049100	1.20534300	-2.26806100
C	11.40369400	2.40820400	-2.20715800
C	10.49487100	0.59483900	-3.52155500
C	11.93964500	2.97920900	-3.35565200
H	11.53361000	2.90983000	-1.25312900
C	11.03266600	1.16706400	-4.67372200
H	9.95501500	-0.34405000	-3.59460600
C	11.76134400	2.36530800	-4.60862300
H	12.49435400	3.90965800	-3.29615600
H	10.89231400	0.67396900	-5.63225000
C	11.06687000	0.06985600	2.60541000
C	10.42482900	0.30153200	3.83926500
C	12.45678100	-0.13697300	2.60602600
C	11.14481900	0.32464900	5.02813900
H	9.35541400	0.48765500	3.86113400
C	13.17922800	-0.11425400	3.79841300
H	12.97377600	-0.33925500	1.67324300
C	12.53579900	0.11556900	5.02487500
H	10.64001800	0.51317600	5.96974600
H	14.25254300	-0.28487300	3.77736800
C	3.09277000	-3.02809800	-0.02521800
H	2.98514200	-3.93369700	0.58152700
C	12.31405100	2.94114100	-5.84816600
H	12.10579200	2.36149100	-6.75710400
C	13.33234800	0.13069200	6.26537000
H	14.40716000	-0.04335500	6.12401100
N	2.07834900	-2.54975900	-0.69512100
N	12.98800000	4.03191800	-5.87343900
N	12.81948400	0.32951000	7.42387600
C	0.94087300	-3.24048400	-0.80923000
N	-0.31033600	-2.72137000	-0.91213100
N	0.72821300	-4.58068400	-0.92028300
C	-1.16404100	-3.76941300	-1.09534600
N	-0.61661600	-4.93668200	-1.12300900
N	-2.31028600	-2.96103700	-1.22068100
C	-3.62349400	-3.23400200	-1.59596100
H	-3.72930200	-4.12835600	-2.19799900
H	13.54475700	0.29945000	8.14267900
C	-4.73320300	-2.43906600	-1.23959100
C	-4.68091300	-1.34808300	-0.32458000

C	-5.99999400	-2.75464600	-1.81529500
C	-5.82067700	-0.62019600	-0.02612700
H	-3.75143100	-1.09061600	0.16809400
C	-7.12921800	-2.01931800	-1.50381000
H	-6.07198700	-3.57782600	-2.52011700
C	-7.07103000	-0.92829700	-0.60673900
H	-5.75042700	0.18687900	0.69616500
H	-8.07025600	-2.27318500	-1.98122900
C	-8.27998900	-0.13787700	-0.28170300
C	-8.19437400	1.24924800	-0.07651000
C	-9.53552900	-0.75861400	-0.17329000
C	-9.33142100	2.01146000	0.22930900
H	-7.23173200	1.74255300	-0.15953600
C	-10.68813800	-0.02086000	0.13436800
H	-9.61636500	-1.82946000	-0.32690400
C	-10.57213100	1.36366000	0.33327500
C	-9.22481900	3.47857500	0.43730900
C	-12.00807900	-0.69310900	0.24828200
H	-11.45781700	1.94342800	0.57111400
C	-8.37744400	4.26204000	-0.36481700
C	-9.97286400	4.12195500	1.44489500
C	-12.12293900	-1.96162500	0.85364500
C	-13.17478900	-0.08245300	-0.24277000
C	-8.28196200	5.63900700	-0.16744700
H	-7.80715200	3.79688900	-1.16273400
C	-9.87779400	5.49469000	1.64237100
H	-10.61714200	3.53452000	2.09183800
C	-13.35570500	-2.59443100	0.96416200
H	-11.23923100	-2.44322200	1.26089300
C	-14.41152700	-0.71682300	-0.13241900
H	-13.11310300	0.88377400	-0.73354500
C	-9.02932900	6.27529600	0.83643400
H	-7.62705600	6.22730200	-0.80514500
H	-10.45250900	5.97559900	2.42691700
C	-14.52095000	-1.97974200	0.47115500
H	-13.43071600	-3.56625000	1.44061700
H	-15.30006800	-0.23003400	-0.52635400
C	-8.90350200	7.73316500	1.01401000
C	-15.84544800	-2.61903100	0.56991500
H	-8.20800800	8.22248900	0.31938400
N	-9.55197800	8.38886900	1.90538700
H	-16.67184500	-2.03184400	0.14810100
N	-16.02977100	-3.76972700	1.10563700
H	-17.01886000	-4.02283300	1.07051000
H	13.27581900	4.24897500	-6.82928800
H	-9.31828000	9.38206800	1.85492700
C	-1.50236400	-1.80056100	-1.10918100
O	-1.63632700	-0.62618100	-1.13212700
H	1.43699400	-5.30151300	-0.98245700

Sum of electronic and thermal Free Energies = -2764.020541 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 449.75 nm.

Table S17: DFT-optimized geometry of ***CO** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	8.25537300	-0.49171900	-0.18856900
C	9.24429600	-1.08375900	0.61423700
C	10.47358000	-0.44800300	0.84273000
C	10.70797700	0.80346200	0.25234600
C	9.73901500	1.41866600	-0.55529000
C	8.51797700	0.76123100	-0.76641700
H	9.05377600	-2.04989600	1.06944900
H	11.65516800	1.30413800	0.42356200
H	7.76424300	1.22966200	-1.39042700
C	6.96136100	-1.17564700	-0.42092100
C	6.89601400	-2.57651300	-0.56473300
C	5.75620200	-0.44278600	-0.50483900
C	5.68378700	-3.21742600	-0.78303000
H	7.80753800	-3.16457600	-0.52995800
C	4.54174400	-1.07529800	-0.72066000
H	5.77458200	0.63462000	-0.37356500
C	4.47752300	-2.48283100	-0.86525900
H	5.66126600	-4.29738800	-0.90183000
H	3.62597100	-0.49631700	-0.77134500
C	10.00248400	2.74217300	-1.17641500
C	10.68619100	3.75042200	-0.46598800
C	9.57785700	3.02289600	-2.48639700
C	10.93525900	4.99060500	-1.04247100
H	11.00421500	3.56448800	0.55529400
C	9.82761800	4.26654500	-3.06525200
H	9.06946800	2.25780600	-3.06473100
C	10.50898400	5.26727400	-2.35420600
H	11.45442200	5.76017700	-0.48095200
H	9.49788800	4.45937800	-4.08294500
C	11.50880600	-1.08875300	1.69403800
C	11.15006600	-1.78603000	2.86618500
C	12.87037900	-1.01732600	1.35299300
C	12.11448100	-2.38895300	3.66535900
H	10.10674000	-1.83504500	3.16248100
C	13.83817100	-1.62218900	2.15409300
H	13.17360500	-0.50581200	0.44482700
C	13.47607000	-2.31635800	3.31953100
H	11.82527400	-2.91492600	4.56911700
H	14.88490000	-1.56193200	1.86701800
C	3.24112500	-3.18135300	-1.09032100
H	3.30403900	-4.26868000	-1.19091300
C	10.75575900	6.56918700	-2.99982900
H	10.36987500	6.65490800	-4.02427400
C	14.52675700	-2.94457500	4.14050500
H	15.54801200	-2.81452100	3.75862600
N	2.08073400	-2.55097400	-1.15115200
N	11.37213100	7.53316000	-2.42017800
N	14.27863200	-3.59495400	5.21779700

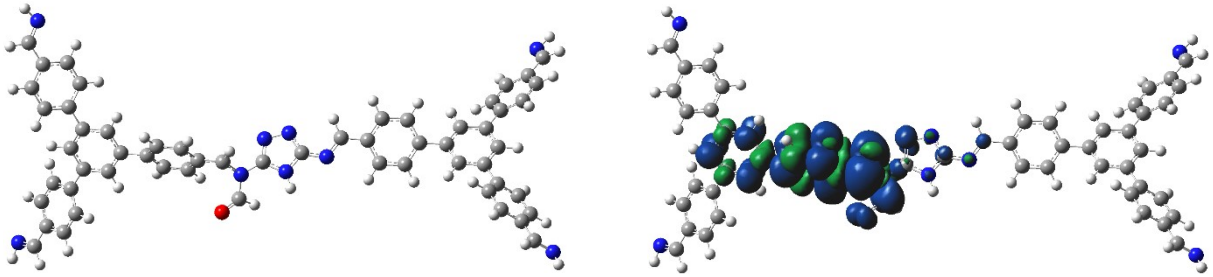
C	0.96771200	-3.21188100	-1.41795900
N	-0.28747600	-2.70441200	-1.39170500
N	0.76406900	-4.59319400	-1.70011300
C	-1.14467900	-3.71007500	-1.75255500
N	-0.62476000	-4.85373800	-1.99713500
N	-2.28247900	-2.87611400	-1.70132600
C	-3.59820600	-3.11617600	-2.00783900
H	-3.74477900	-3.97331100	-2.65398100
H	15.14593600	-3.94562400	5.62811800
C	-4.69549600	-2.35514800	-1.54394100
C	-4.61565800	-1.33601600	-0.54919700
C	-5.99169200	-2.63512700	-2.07362700
C	-5.74849600	-0.65018800	-0.13720200
H	-3.66429000	-1.09947500	-0.08921600
C	-7.11201700	-1.94551700	-1.64577100
H	-6.09482300	-3.39775000	-2.84091600
C	-7.02698700	-0.92686000	-0.66816800
H	-5.64391500	0.09779500	0.64332800
H	-8.07163700	-2.17795300	-2.09784100
C	-8.22651700	-0.18948200	-0.21650900
C	-8.14479900	1.16429700	0.15684100
C	-9.48108200	-0.82216900	-0.14868900
C	-9.27390000	1.87483200	0.58952400
H	-7.18789900	1.67297400	0.10740700
C	-10.62739300	-0.13412800	0.27481000
H	-9.56583500	-1.86703100	-0.42765700
C	-10.51181300	1.21523000	0.64400500
C	-9.16314100	3.30394800	0.98058000
C	-11.94254200	-0.82287100	0.33415900
H	-11.39188200	1.75583400	0.97612700
C	-8.33809300	4.18859700	0.26473700
C	-9.88448200	3.80976600	2.08201500
C	-12.04089700	-2.15887600	0.77551000
C	-13.12257600	-0.16142800	-0.04764300
C	-8.23775900	5.52882000	0.63607300
H	-7.78860300	3.83270500	-0.60107600
C	-9.78505400	5.14579200	2.45282500
H	-10.51127200	3.14127100	2.66424000
C	-13.26908000	-2.80750100	0.83243200
H	-11.14669100	-2.68374600	1.09736800
C	-14.35490300	-0.81119900	0.00936400
H	-13.07462500	0.85985000	-0.41228500
C	-8.95830100	6.02756400	1.73315500
H	-7.59979000	6.19684700	0.06294100
H	-10.33940900	5.51856300	3.30771300
C	-14.44737100	-2.14156100	0.44877500
H	-13.33004800	-3.83269800	1.18233200
H	-15.25368000	-0.28281800	-0.29856200
C	-8.82766000	7.45021600	2.09501900
C	-15.76751300	-2.79499000	0.49442800
H	-8.15156200	8.02810400	1.45100700
N	-9.45001500	7.98267300	3.08230600
H	-16.60440200	-2.16276500	0.16938200
N	-15.93798000	-4.00609000	0.88129300
H	-16.92719100	-4.25683300	0.83510300
H	11.43366000	8.34033500	-3.04328100

H	-9.21691600	8.97461000	3.15489500
C	-1.42992000	-1.77046700	-1.40779600
O	-1.55979900	-0.59546200	-1.18318300
H	1.38981900	-5.04783900	-2.36026900

Sum of electronic and thermal Free Energies = -2764.161018 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 441.23 nm.

Table S18: DFT-optimized geometry of ***CHO** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)



Spin Density Distribution

Atom	x	y	z
C	-8.97481500	-0.28654800	0.02238400
C	-9.71104700	-1.29206400	-0.62309900
C	-11.11066700	-1.23227100	-0.69903100
C	-11.77292600	-0.14192000	-0.11449100
C	-11.06214000	0.87770600	0.53692100
C	-9.66281400	0.79338000	0.59687900
H	-9.18915400	-2.13044700	-1.07225900
H	-12.85516900	-0.08669400	-0.16735000
H	-9.10370100	1.57647200	1.09807300
C	-7.49430600	-0.36543900	0.09765400
C	-6.84720800	-1.59709800	0.30430600
C	-6.70027900	0.79380400	-0.03660900
C	-5.45879900	-1.66901300	0.37510000
H	-7.43417000	-2.50065200	0.43336700
C	-5.31549100	0.72597600	0.03301000
H	-7.17663300	1.75157600	-0.22068800
C	-4.67146700	-0.51041200	0.24175200
H	-4.97875100	-2.62922100	0.54349700
H	-4.71698000	1.62334100	-0.08190200
C	-11.77857200	2.02471600	1.15167800
C	-12.89671300	2.60292800	0.51580100
C	-11.36131200	2.56192000	2.38153400
C	-13.57150600	3.67535100	1.08754700
H	-13.22403400	2.22046700	-0.44614700

C	-12.03795700	3.63745900	2.95556400
H	-10.51735100	2.12284100	2.90421500
C	-13.15154200	4.20890000	2.31948800
H	-14.42494100	4.11587800	0.58297000
H	-11.70344500	4.03202700	3.91166800
C	-11.87746000	-2.30447700	-1.38391700
C	-11.39829300	-2.88743400	-2.57526400
C	-13.09862400	-2.76463700	-0.86224100
C	-12.11229200	-3.89095400	-3.21993000
H	-10.46854300	-2.53276200	-3.00947900
C	-13.81493700	-3.77148600	-1.50815700
H	-13.48032000	-2.34966200	0.06533400
C	-13.33396300	-4.34896600	-2.69406900
H	-11.73655800	-4.32461300	-4.14077600
H	-14.75313200	-4.11848400	-1.08263200
C	-3.22172300	-0.63089700	0.32476900
H	-2.82518600	-1.64046800	0.47775200
C	-13.84281200	5.34314400	2.95846600
H	-13.41447900	5.66028500	3.91851000
C	-14.11888500	-5.41131900	-3.34823900
H	-15.05171800	-5.67689000	-2.83356600
N	-2.43149200	0.38781500	0.22914300
N	-14.86518100	5.92116200	2.44297400
N	-13.75034000	-5.98722300	-4.43335900
C	-1.07235800	0.17458100	0.26660700
N	-0.21345500	1.22521800	0.47972600
N	-0.37312800	-0.93636200	0.08284100
C	1.03570400	0.68077900	0.41686200
H	-0.48022500	2.17242400	0.71577900
N	0.96280000	-0.61249400	0.17633200
N	2.22774400	1.39092200	0.61644500
C	3.19629200	0.78055300	1.44900500
H	2.79136300	0.32146000	2.34361000
H	-14.43700000	-6.69021500	-4.71240100
C	4.56704900	0.66330000	1.13786800
C	5.13762400	1.01671200	-0.11888400
C	5.44488800	0.12052200	2.12328600
C	6.49041000	0.84462000	-0.35910600
H	4.50457500	1.40156500	-0.90925200
C	6.79556100	-0.04287300	1.87019600
H	5.04292400	-0.15655600	3.09386000
C	7.35802500	0.31768900	0.62448700
H	6.88334400	1.09547000	-1.33956900
H	7.43469400	-0.43388400	2.65571400
C	8.80340500	0.14166900	0.35542700
C	9.50251800	1.06257600	-0.44303600
C	9.50654300	-0.95068600	0.89121100
C	10.87119000	0.90728900	-0.70799900
H	8.97484900	1.91238100	-0.86282600
C	10.87549800	-1.12957900	0.64338600
H	8.98087600	-1.67287100	1.50680800
C	11.54659600	-0.19350600	-0.15864000
C	11.59314000	1.89087200	-1.55559500
C	11.60243300	-2.29053200	1.21857200
H	12.60524800	-0.32358200	-0.35745400
C	11.31924900	3.26610800	-1.46029800

C	12.57154500	1.46811700	-2.47918200
C	10.99719800	-3.56271400	1.28312700
C	12.91102400	-2.15110300	1.71210200
C	11.99784900	4.18510300	-2.25967800
H	10.58739700	3.62223200	-0.74208900
C	13.24833700	2.38381900	-3.27657800
H	12.78488300	0.40902000	-2.58663200
C	11.67352500	-4.65227900	1.81956300
H	9.99548600	-3.70024500	0.88767300
C	13.58990100	-3.24357300	2.25040700
H	13.39328100	-1.17874700	1.69558700
C	12.97062900	3.75935300	-3.17827100
H	11.77559400	5.24485000	-2.16380300
H	13.99219300	2.04355900	-3.98933500
C	12.98322300	-4.50828400	2.31227600
H	11.19872500	-5.62713000	1.85507400
H	14.59847200	-3.11153800	2.63389600
C	13.66625100	4.75998800	-4.00727500
C	13.73256700	-5.63978200	2.88720200
H	13.35732900	5.79875900	-3.83027900
N	14.56329900	4.45304800	-4.87119500
H	14.74209500	-5.39052800	3.23997200
N	13.25338200	-6.82648000	2.97334800
H	13.93635500	-7.45427300	3.40113000
H	-15.18608700	6.67965300	3.04741200
H	14.91352400	5.29441900	-5.33271800
C	2.35794900	2.66718500	0.07787800
O	3.28278000	3.42529300	0.32082100
H	1.53543300	2.92155300	-0.60747700

Sum of electronic and thermal Free Energies = -2764.859808 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 428.69 nm.

Table S19: DFT-optimized geometry of ***OCH_2** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.28152000	0.23300100	-0.05091900
C	-8.73154400	1.49951100	0.35281500
C	-10.08693900	1.73485200	0.62915100
C	-10.99802800	0.67607200	0.49370700
C	-10.57578800	-0.60011300	0.09089900
C	-9.21416900	-0.80804100	-0.17645000
H	-8.01836300	2.31081600	0.45472500
H	-12.04842100	0.84767700	0.70467500
H	-8.87713200	-1.79154100	-0.48669000
C	-6.84430900	-0.00194300	-0.33942000
C	-6.07119400	0.96971500	-0.99960100
C	-6.21880200	-1.20802900	0.04216500

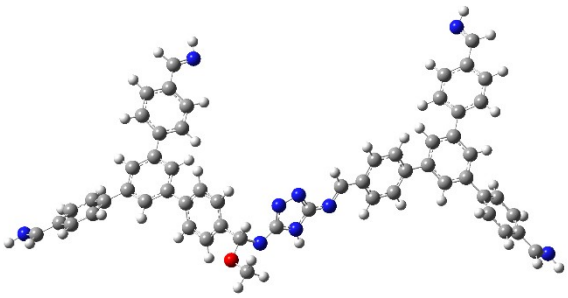
C	-4.72328600	0.74573400	-1.26853800
H	-6.53242400	1.89667600	-1.32509300
C	-4.87532400	-1.43475100	-0.22479600
H	-6.79009300	-1.96320500	0.57286500
C	-4.10372700	-0.45827400	-0.88640600
H	-4.14606500	1.50618200	-1.78762800
H	-4.40567000	-2.36324400	0.08185100
C	-11.55161600	-1.71126400	-0.04972600
C	-12.60482500	-1.86998600	0.87455900
C	-11.44951800	-2.63231100	-1.10636200
C	-13.51942100	-2.90926900	0.74810300
H	-12.69118300	-1.18410700	1.71172100
C	-12.36672700	-3.67459600	-1.23392100
H	-10.66250600	-2.52117600	-1.84564700
C	-13.41348200	-3.82905400	-0.31101000
H	-14.31943300	-3.02425500	1.47191300
H	-12.27396000	-4.37081600	-2.06353700
C	-10.54887400	3.08002900	1.05794500
C	-9.77744900	3.85995600	1.94416100
C	-11.76532200	3.60867700	0.59313800
C	-10.20550200	5.11870900	2.34984400
H	-8.84519100	3.46355300	2.33464400
C	-12.19509300	4.87134000	0.99961900
H	-12.36873900	3.03991600	-0.10736600
C	-11.42357300	5.64419300	1.88205300
H	-9.60629900	5.70448600	3.03892700
H	-13.13537400	5.26448800	0.62146000
C	-2.68905200	-0.65205400	-1.18552000
H	-2.18559200	0.16672000	-1.71126000
C	-14.36274400	-4.94408600	-0.47942600
H	-14.16899200	-5.58470900	-1.34995000
C	-11.90985600	6.97463800	2.28966500
H	-12.87256700	7.26696500	1.84986800
N	-2.04981700	-1.72410900	-0.85250800
N	-15.34121400	-5.15926000	0.32142200
N	-11.26682400	7.73885900	3.09441100
C	-0.72416500	-1.85162300	-1.20640400
N	0.04023700	-2.85631800	-0.64913100
N	0.00414500	-1.16976900	-2.06951600
C	1.27167500	-2.72733600	-1.21915100
H	-0.25657100	-3.50434600	0.06815900
N	1.27509800	-1.72668500	-2.08569200
N	2.35830700	-3.49697400	-0.87557600
C	3.53089300	-3.59355600	-1.77731100
H	3.25974800	-3.44226300	-2.83114300
H	-11.77925900	8.61022600	3.24164300
C	4.74279000	-2.79321600	-1.41069200
C	5.22257400	-2.79217500	-0.09355600
C	5.41630100	-2.04641800	-2.38272800
C	6.35646900	-2.05825600	0.24206000
H	4.69605500	-3.35921700	0.66809600
C	6.55306200	-1.30901400	-2.04703600
H	5.05575600	-2.04303800	-3.40791000
C	7.04214400	-1.30294300	-0.73001400
H	6.70193300	-2.05011100	1.27121000
H	7.07440700	-0.75181200	-2.81907900

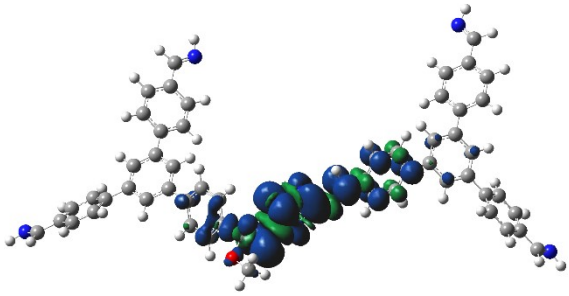
C	8.25272500	-0.51918200	-0.36996000
C	9.20239200	-1.04150300	0.52089200
C	8.46656300	0.75586000	-0.91490900
C	10.35060000	-0.31349800	0.86909000
H	9.04565800	-2.02601900	0.94929200
C	9.60616500	1.50563000	-0.58530500
H	7.73756600	1.16906900	-1.60426300
C	10.53964000	0.95892200	0.30850400
C	11.34697500	-0.87937100	1.81446300
C	9.82031500	2.85320400	-1.17249400
H	11.42354000	1.53081200	0.57098200
C	11.68899400	-2.24202600	1.77406800
C	11.97428000	-0.06246600	2.77789000
C	8.74194700	3.74516700	-1.34714000
C	11.10162100	3.27327000	-1.56894700
C	12.62321700	-2.76900800	2.66490500
H	11.23935500	-2.88978000	1.02805900
C	12.90559600	-0.58731800	3.66648500
H	11.71023600	0.98861600	2.84287500
C	8.93701100	5.00705000	-1.89664100
H	7.74666300	3.45173300	-1.02767300
C	11.29782000	4.53867400	-2.12062000
H	11.94633500	2.59927900	-1.46674200
C	13.24443400	-1.95193600	3.62290800
H	12.87858200	-3.82423400	2.61080300
H	13.37378500	0.05095000	4.40849700
C	10.22099700	5.42294700	-2.29313900
H	8.09997700	5.68669300	-2.01725200
H	12.29591300	4.83974400	-2.42855400
C	14.22602200	-2.54503000	4.54874400
C	10.46649900	6.75190200	-2.88128800
H	14.40282200	-3.61924600	4.40537500
N	14.83185400	-1.86896500	5.45489800
H	11.51278500	6.95000300	-3.14936000
N	9.53827700	7.61670800	-3.07025300
H	9.92425400	8.46577600	-3.48700900
H	-15.87083300	-5.97968000	0.02132600
H	15.46557000	-2.47172100	5.98278400
C	2.34403300	-4.97253900	-0.81809000
O	3.63068700	-5.01424100	-1.46257500
H	1.55066300	-5.43309300	-1.42395500
H	2.36568500	-5.39445900	0.19069300

Sum of electronic and thermal Free Energies = -2765.440026 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 566.57 nm.

Table S20: DFT-optimized geometry of ***OCH$_3$** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)





Spin Density Distribution

Atom	x	y	z
C	-7.44933200	-0.15539300	-0.21639000
C	-7.87634000	1.16245200	-0.44235000
C	-9.16444500	1.58059000	-0.07624700
C	-10.03099800	0.65310600	0.52240800
C	-9.63090100	-0.67112000	0.75814900
C	-8.33578900	-1.06147100	0.38614800
H	-7.19817500	1.87120000	-0.90577200
H	-11.02960800	0.96621300	0.80866100
H	-8.01611900	-2.08254600	0.56534900
C	-6.08441900	-0.58422600	-0.60896800
C	-5.49598100	-0.11818500	-1.79958000
C	-5.34443900	-1.47125500	0.20358400
C	-4.21689800	-0.52275000	-2.16637500
H	-6.05261300	0.54556700	-2.45293300
C	-4.06852200	-1.87732900	-0.15771800
H	-5.76982300	-1.82364200	1.13775800
C	-3.48263000	-1.40873300	-1.35321400
H	-3.78279800	-0.15957500	-3.09384200
H	-3.50657400	-2.55141500	0.47953200
C	-10.56116100	-1.64172600	1.38993100
C	-11.41322000	-1.24647600	2.44179300
C	-10.61538100	-2.97714800	0.95543500
C	-12.28545000	-2.15125100	3.03598300
H	-11.37293800	-0.22578700	2.80964000
C	-11.49012800	-3.88497200	1.55099800
H	-9.98715900	-3.30335100	0.13251400
C	-12.33697200	-3.48692200	2.59768400
H	-12.92928600	-1.83627300	3.85047300
H	-11.52206600	-4.91106800	1.19363700
C	-9.60356500	2.97874600	-0.31941000
C	-8.71864800	4.05876900	-0.12157600
C	-10.91073600	3.26003300	-0.75219500
C	-9.12495500	5.36888500	-0.34731500
H	-7.71077900	3.86804300	0.23421600
C	-11.31865100	4.57389200	-0.97900700
H	-11.60620800	2.44680100	-0.93449800
C	-10.43422100	5.64605800	-0.78058300
H	-8.43664200	6.19118800	-0.18259700
H	-12.33174200	4.76842100	-1.32166200
C	-2.15288800	-1.80697700	-1.77332500
H	-1.79030900	-1.38724300	-2.71691100

C	-13.24925600	-4.47452500	3.20200300
H	-13.18804800	-5.48203100	2.76969700
C	-10.90159800	7.02159900	-1.03011300
H	-11.94448500	7.09932300	-1.36466300
N	-1.41782700	-2.62002800	-1.07462200
N	-14.05553900	-4.18985500	4.15792700
N	-10.15686500	8.05373600	-0.87191100
C	-0.17781700	-2.95059300	-1.53837300
N	0.64167200	-3.76895400	-0.83740300
N	0.43747800	-2.57638600	-2.68633600
C	1.80781400	-3.90084100	-1.57806700
H	0.44542700	-4.19748200	0.05737100
N	1.64619600	-3.14611100	-2.72326200
N	2.82130000	-4.62834900	-1.18715100
C	4.01423600	-4.64232100	-2.03065900
H	3.75301700	-4.50180300	-3.09046200
H	-10.67629100	8.90374700	-1.09833900
C	4.94518100	-3.53123400	-1.58132900
C	5.70744300	-3.66628200	-0.41357800
C	5.01054800	-2.33373700	-2.30158700
C	6.52856700	-2.62519600	0.01730500
H	5.65495500	-4.58862200	0.15509400
C	5.83046700	-1.29104300	-1.86833000
H	4.41965300	-2.21615100	-3.20503000
C	6.60411100	-1.41771200	-0.70119700
H	7.09909000	-2.74252900	0.93379100
H	5.88758700	-0.38026400	-2.45667900
C	7.47852200	-0.30760700	-0.24037000
C	8.74925700	-0.57218500	0.29248400
C	7.04933400	1.02536600	-0.32997900
C	9.58544600	0.46588700	0.73176000
H	9.09107700	-1.59928100	0.36718700
C	7.86476000	2.08360100	0.10009900
H	6.06858300	1.24130700	-0.74101500
C	9.13041500	1.78942300	0.63014000
C	10.92905500	0.16894100	1.29151500
C	7.39628700	3.48945100	-0.00478900
H	9.76853000	2.59977200	0.96690900
C	11.73575400	-0.83979000	0.73715600
C	11.42976000	0.89262800	2.39366500
C	6.05365200	3.82612800	0.26577800
C	8.27743800	4.51942600	-0.37672800
C	12.99651300	-1.11500300	1.26509400
H	11.38573700	-1.39773100	-0.12565900
C	12.68665000	0.61868400	2.92057400
H	10.81607100	1.66130700	2.85326100
C	5.60956500	5.13967300	0.16737600
H	5.35939000	3.05174800	0.57730900
C	7.83273200	5.83723200	-0.47523300
H	9.31111100	4.28672700	-0.61256400
C	13.49069800	-0.39163400	2.36227900
H	13.60698500	-1.89387000	0.81530500
H	13.05549500	1.17744400	3.77434000
C	6.49474400	6.16710000	-0.20633400
H	4.57584800	5.38528600	0.38673100
H	8.52943200	6.61677300	-0.77290000

C	14.82816700	-0.71112200	2.89268200
C	6.06113400	7.57079700	-0.32381500
H	15.35062600	-1.52038900	2.36545400
N	15.35072000	-0.09866200	3.89124900
H	6.85222800	8.27256900	-0.61949400
N	4.85731600	7.95384200	-0.10138600
H	4.77494400	8.96267700	-0.23970100
H	-14.59390700	-5.01574800	4.42564300
H	16.27842700	-0.47594200	4.09269900
C	3.95905100	-6.98994800	-2.41182900
O	4.68240700	-5.88170200	-1.87155600
H	3.77249600	-6.85024100	-3.48616900
H	4.58478900	-7.87221500	-2.26572500
H	3.00188100	-7.13248000	-1.89600100

Sum of electronic and thermal Free Energies = -2766.032888 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 514.3 nm.

Table S21: DFT-optimized geometry of ***CH_3OH** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-9.11465800	-0.29100500	0.17251000
C	-10.05576700	-1.27842600	-0.15763800
C	-11.39866300	-0.95047000	-0.39790900
C	-11.79386100	0.39263800	-0.30199100
C	-10.87425100	1.40025200	0.02679400
C	-9.53722100	1.04438900	0.26016100
H	-9.73933400	-2.31374200	-0.22953000
H	-12.82997800	0.65668800	-0.48605500
H	-8.81801100	1.81597100	0.51411900
C	-7.69714200	-0.65226000	0.42554000
C	-7.36443000	-1.82943100	1.11946700
C	-6.64845100	0.17889800	-0.02311400
C	-6.03400400	-2.16413100	1.35765000
H	-8.15147600	-2.47505300	1.49561400
C	-5.32090800	-0.15124600	0.21323800
H	-6.88053700	1.08050500	-0.58115000
C	-4.99176000	-1.33148600	0.91005000
H	-5.79877500	-3.07385200	1.90357500
H	-4.52480000	0.49338000	-0.14359600
C	-11.30760500	2.81771600	0.12525800
C	-12.24125600	3.35319100	-0.78604400
C	-10.79769400	3.66075300	1.12753100
C	-12.64808400	4.67960700	-0.69922300
H	-12.63239000	2.72762800	-1.58255100
C	-11.20541600	4.99120400	1.21506600
H	-10.09520000	3.26945000	1.85665700
C	-12.13457200	5.52010800	0.30509100

H	-13.36029300	5.08133900	-1.41231100
H	-10.80424300	5.62343100	2.00306900
C	-12.38427100	-2.00557900	-0.74721800
C	-12.03178000	-3.06805800	-1.60490800
C	-13.69195100	-1.97123100	-0.23339600
C	-12.95078100	-4.05699600	-1.93626800
H	-11.03441400	-3.10359700	-2.03234800
C	-14.61411900	-2.96297400	-0.56530300
H	-13.98413500	-1.17751400	0.44702100
C	-14.25866000	-4.01882100	-1.41975300
H	-12.66896600	-4.86396100	-2.60451500
H	-15.61778100	-2.92138600	-0.14984100
C	-3.61232400	-1.71755100	1.18263900
H	-3.46884700	-2.64735400	1.74358100
C	-12.54088200	6.93165700	0.42795000
H	-12.06647500	7.47647100	1.25487900
C	-15.26028100	-5.04904900	-1.74850200
H	-16.24266300	-4.90151600	-1.28074500
N	-2.60340400	-1.01208300	0.78949300
N	-13.38137500	7.48984000	-0.36392600
N	-15.01410400	-6.04407500	-2.51946800
C	-1.33097700	-1.42429700	1.11966500
N	-0.23979100	-0.82990200	0.55165700
N	-0.92550700	-2.35365600	1.98053200
C	0.85180200	-1.44555600	1.09756800
H	-0.23956700	-0.09092600	-0.13930800
N	0.44674200	-2.36890400	1.96364900
N	2.12311200	-1.07529800	0.71559200
C	3.13963900	-1.62680300	1.29050100
H	3.01040500	-2.37347000	2.08118300
H	-15.84287900	-6.63391300	-2.61292500
C	4.51381800	-1.29304900	0.93014500
C	4.82126000	-0.34801000	-0.06897300
C	5.57102700	-1.92951300	1.60601300
C	6.14222100	-0.04582200	-0.37041700
H	4.01322700	0.14269000	-0.60046400
C	6.89651500	-1.62674300	1.29978900
H	5.35366100	-2.65455000	2.38536100
C	7.20698900	-0.67507300	0.30968200
H	6.35831500	0.67639700	-1.15110000
H	7.69546700	-2.10961700	1.85303300
C	8.61645700	-0.32409000	0.00644900
C	8.97663800	1.00933000	-0.23814400
C	9.61085000	-1.31298100	-0.02666400
C	10.30672600	1.36508500	-0.50602500
H	8.21443200	1.78068400	-0.21582700
C	10.94784600	-0.98663000	-0.30031400
H	9.34156300	-2.34690000	0.16234400
C	11.28145800	0.35610100	-0.53624600
C	10.67342100	2.78383300	-0.74833500
C	11.99112600	-2.04334100	-0.33797200
H	12.31325200	0.61865900	-0.74510800
C	10.07708600	3.81833900	-0.00683000
C	11.62847500	3.12822000	-1.72696800
C	11.72074500	-3.30372700	-0.90979400
C	13.27215900	-1.81406300	0.19260400

C	10.42303500	5.14934400	-0.23595300
H	9.35582300	3.58098300	0.76892900
C	11.97358300	4.45529500	-1.95571200
H	12.08631600	2.34820500	-2.32759100
C	12.69350000	-4.29582000	-0.95033200
H	10.74538700	-3.49639200	-1.34606000
C	14.24814500	-2.80909300	0.15252000
H	13.50101200	-0.86116000	0.65946400
C	11.37457800	5.48771200	-1.21130300
H	9.95561400	5.93320100	0.35449500
H	12.70396000	4.70688100	-2.71752500
C	13.97451600	-4.06226800	-0.41833700
H	12.47539500	-5.25816200	-1.40134900
H	15.22990200	-2.61364100	0.57638800
C	11.71516700	6.90603800	-1.42394900
C	15.03081900	-5.09006100	-0.44326600
H	11.18121000	7.60982800	-0.77177400
N	12.56688000	7.29831200	-2.29898500
H	15.98385000	-4.78132900	0.00611000
N	14.86024100	-6.25668200	-0.94816300
H	15.71525700	-6.80898200	-0.86185200
H	-13.51949100	8.46764000	-0.10239700
H	12.65198300	8.31616700	-2.27993400
C	5.83103800	2.39449100	2.19215800
O	6.50617200	1.42097900	2.99585000
H	4.81717900	2.06962900	1.92755000
H	5.76727000	3.30863100	2.78679200
H	6.38330600	2.61281000	1.26916800
H	6.57433500	0.59777900	2.49161000

Sum of electronic and thermal Free Energies = -2766.670015 (Hartree/Particle).

Table S22: DFT-optimized geometry of ***O** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-8.89052400	-0.17727200	0.16817400
C	-9.63908600	-1.31933700	-0.15582400
C	-11.00268900	-1.22781300	-0.47307500
C	-11.61600100	0.03434600	-0.46123000
C	-10.89180100	1.19272500	-0.14040000
C	-9.52908400	1.07243700	0.17120200
H	-9.15489100	-2.29018600	-0.16302300
H	-12.67004400	0.11574800	-0.70530300
H	-8.95980900	1.96194000	0.41960600
C	-7.44826300	-0.28858000	0.50139200
C	-6.96309800	-1.36952700	1.25941000
C	-6.52895300	0.68961800	0.06508300
C	-5.60997200	-1.47025400	1.57081700
H	-7.65162900	-2.12341500	1.62703800

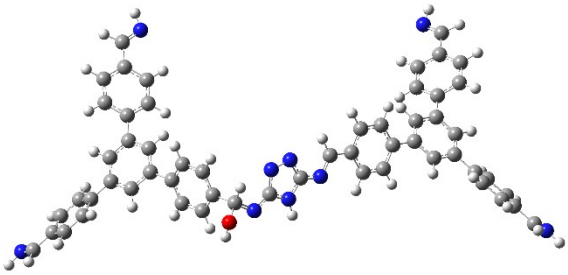
C	-5.17939500	0.59334900	0.37467900
H	-6.87714600	1.51994300	-0.54099600
C	-4.69772600	-0.49139200	1.13524600
H	-5.25670400	-2.30843300	2.16525500
H	-4.48273400	1.34835800	0.02655700
C	-11.55464800	2.52214900	-0.13306800
C	-12.51022700	2.85824000	-1.11424700
C	-11.24562000	3.47830000	0.84954400
C	-13.13173800	4.10166400	-1.11354500
H	-12.74896000	2.14449100	-1.89674000
C	-11.86892900	4.72552300	0.85085600
H	-10.53080300	3.23888400	1.63057400
C	-12.81929700	5.05586700	-0.12833000
H	-13.85827800	4.35023700	-1.87998900
H	-11.62109600	5.44724900	1.62500200
C	-11.78289100	-2.44489700	-0.81465300
C	-11.21682700	-3.46862500	-1.60223900
C	-13.10361700	-2.60662900	-0.36225900
C	-11.94307800	-4.60908500	-1.92518700
H	-10.20599000	-3.35600200	-1.98211000
C	-13.83230800	-3.75058500	-0.68548800
H	-13.55682400	-1.84493000	0.26438100
C	-13.26463800	-4.76717300	-1.47001000
H	-11.49860000	-5.38486200	-2.53971200
H	-14.84940400	-3.85941200	-0.31763100
C	-3.29063400	-0.63266600	1.48596800
H	-3.02365200	-1.50902900	2.08636700
C	-13.45636200	6.38468400	-0.09475100
H	-13.12376300	7.03316600	0.72656000
C	-14.06587500	-5.96189200	-1.79152800
H	-15.08244000	-5.95880600	-1.37650400
N	-2.39346900	0.22088500	1.11449100
N	-14.33136000	6.76392700	-0.95243300
N	-13.62051900	-6.93414700	-2.49963100
C	-1.09351800	0.03742000	1.52820600
N	-0.07833100	0.75426800	0.95931900
N	-0.59795600	-0.75043300	2.47982200
C	1.05161800	0.35930100	1.60949100
H	-0.15508500	1.42616400	0.20618100
N	0.75855500	-0.54318600	2.52700000
N	2.31022300	0.84701800	1.23166800
C	3.36255800	0.67548700	2.20544000
H	3.12000600	0.08454500	3.08828500
H	-14.33602100	-7.65629500	-2.60047800
C	4.76083200	0.54095900	1.71295300
C	5.22059700	1.29629800	0.62518800
C	5.63538100	-0.34493800	2.35167400
C	6.53413000	1.16257400	0.18507800
H	4.54343900	1.98118300	0.12521800
C	6.95209200	-0.47822900	1.90872400
H	5.29285900	-0.92711700	3.20284700
C	7.42396000	0.27325900	0.81927500
H	6.86954100	1.73839300	-0.67181000
H	7.62294900	-1.15332700	2.43055300
C	8.82820500	0.13885100	0.35089900
C	9.55543000	1.26783600	-0.05505500

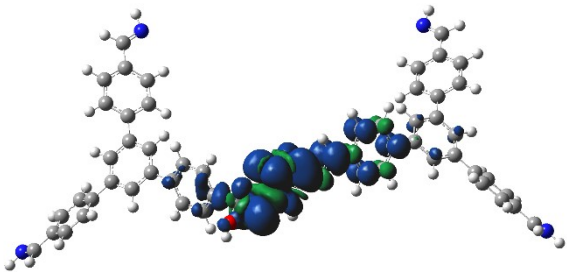
C	9.45156600	-1.11738400	0.31033600
C	10.88360900	1.15801000	-0.49478300
H	9.08245400	2.24396000	-0.02823000
C	10.77861500	-1.25682900	-0.12462600
H	8.89771700	-1.99659000	0.62268500
C	11.48227700	-0.11069700	-0.52532500
C	11.64201600	2.36348600	-0.91717100
C	11.42740900	-2.59279600	-0.15729100
H	12.50845900	-0.20750900	-0.86409100
C	11.50578100	3.58025700	-0.22693800
C	12.51853000	2.31734600	-2.02108700
C	10.70776900	-3.73673900	-0.56046200
C	12.77392500	-2.75105700	0.21343500
C	12.21898500	4.70980700	-0.62605600
H	10.85607200	3.63919100	0.64063000
C	13.23000000	3.44326200	-2.41949500
H	12.62396300	1.39474700	-2.58360100
C	11.31044200	-4.98901000	-0.59168800
H	9.67283100	-3.63647000	-0.87277800
C	13.37899200	-4.00682300	0.18208200
H	13.34588000	-1.89214400	0.55017100
C	13.09031400	4.65907500	-1.72581700
H	12.10423300	5.63847200	-0.07283900
H	13.89446500	3.39580700	-3.27593000
C	12.65825600	-5.14276200	-0.21954900
H	10.74751600	-5.85937700	-0.91205600
H	14.41926900	-4.10770400	0.48092700
C	13.82724900	5.87387400	-2.11774400
C	13.33105600	-6.45398800	-0.23874800
H	13.63015500	6.75348400	-1.49066900
N	14.63730900	5.91219800	-3.11142500
H	14.38329000	-6.43538000	0.07462400
N	12.74294800	-7.53786900	-0.59166400
H	13.38872900	-8.32720300	-0.53236200
H	-14.64130400	7.71523300	-0.74617200
H	15.03815600	6.84705700	-3.20611600
O	2.75782800	1.96164400	2.18509400

Sum of electronic and thermal Free Energies = -2726.103223 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 519.74 nm.

Table S23: DFT-optimized geometry of ***OH** (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM. The spin density plot is also shown below. (Isovalue = 0.0004)





Spin Density Distribution

Atom	x	y	z
C	-7.44970000	0.06616300	0.17369100
C	-7.80915600	-1.28948900	0.11829600
C	-9.08938100	-1.68431600	-0.29769200
C	-10.01718600	-0.69517000	-0.65854900
C	-9.68518000	0.66751800	-0.61105800
C	-8.39639700	1.03432300	-0.19540700
H	-7.08393200	-2.04580800	0.39927100
H	-11.01042700	-0.99002700	-0.98058700
H	-8.12883900	2.08496100	-0.15678600
C	-6.09129000	0.46807600	0.61433900
C	-5.44008800	-0.21485400	1.65865800
C	-5.41958600	1.54445100	-0.00603500
C	-4.16498600	0.16064900	2.06743800
H	-5.94440100	-1.02944400	2.16793200
C	-4.14807600	1.92300100	0.39818100
H	-5.89424000	2.06953500	-0.82863300
C	-3.49798600	1.23452000	1.44492300
H	-3.68208600	-0.37359500	2.88096400
H	-3.63842700	2.74475900	-0.09306400
C	-10.67933600	1.70257900	-0.99454600
C	-11.54964700	1.49971400	-2.08547600
C	-10.77711200	2.90921400	-0.28069700
C	-12.48089600	2.46575500	-2.44874800
H	-11.47781000	0.58513900	-2.66612000
C	-11.71111300	3.87838200	-0.64454700
H	-10.13548800	3.08269600	0.57752100
C	-12.57556800	3.67211400	-1.73144600
H	-13.13820900	2.30033000	-3.29591600
H	-11.77555400	4.80102400	-0.07339800
C	-9.45600000	-3.12281600	-0.35287100
C	-8.53069500	-4.08727700	-0.80262800
C	-10.73244400	-3.55844900	0.04200200
C	-8.86839000	-5.43468600	-0.85506400
H	-7.54617200	-3.77219500	-1.13457100
C	-11.07156700	-4.90991300	-0.01023200
H	-11.45707000	-2.84082100	0.41373000
C	-10.14681100	-5.86671700	-0.45802900
H	-8.14973500	-6.16520500	-1.21132100
H	-12.06167300	-5.22619600	0.30803600
C	-2.16835400	1.59209500	1.89980700
H	-1.75126600	0.99450000	2.71647000

C	-13.54993200	4.71988400	-2.08588700
H	-13.51706800	5.61289700	-1.44793100
C	-10.54053900	-7.28668100	-0.49826800
H	-11.56584900	-7.48937800	-0.16161000
N	-1.49201200	2.56867400	1.37172700
N	-14.37577400	4.60775800	-3.06074500
N	-9.75471200	-8.22012800	-0.89335900
C	-0.25544600	2.85656000	1.87017000
N	0.54132500	3.78475200	1.28984200
N	0.37262500	2.34188800	2.95563100
C	1.70709600	3.83703000	2.03968200
H	0.33273000	4.32545800	0.46102700
N	1.56779100	2.92892400	3.06969200
N	2.70774100	4.62773400	1.75304100
C	3.89231400	4.55197000	2.59432400
H	3.65027000	4.29283500	3.62958300
H	-10.22508400	-9.12544100	-0.84133700
C	4.85270900	3.51533700	2.02804300
C	5.29748500	3.59965200	0.70064600
C	5.30424600	2.45850500	2.82516400
C	6.18258200	2.65334700	0.18831600
H	4.93868600	4.39760400	0.05669500
C	6.18820300	1.50767600	2.31175900
H	4.96876400	2.37823300	3.85547900
C	6.64366800	1.58836700	0.98474000
H	6.49813800	2.72616300	-0.84803300
H	6.54287200	0.70879300	2.95595100
C	7.58339400	0.57648100	0.43493600
C	8.62959600	0.96138300	-0.41715700
C	7.43900100	-0.78192900	0.75548300
C	9.52148300	0.01631200	-0.94725800
H	8.74975100	2.00915600	-0.67259700
C	8.31748600	-1.74839600	0.24181400
H	6.63269000	-1.08993200	1.41304900
C	9.35374700	-1.33521900	-0.60953300
C	10.62277100	0.43853300	-1.85034300
C	8.15285500	-3.18311500	0.59004600
H	10.03725800	-2.07424000	-1.01433400
C	11.33788400	1.62500100	-1.61299400
C	10.97786100	-0.34151200	-2.97037400
C	6.87015900	-3.76119900	0.68823300
C	9.27046800	-4.00161000	0.82792200
C	12.36997800	2.01759800	-2.46438300
H	11.10141900	2.23339400	-0.74568800
C	12.00627700	0.04964600	-3.81988800
H	10.42543300	-1.25070300	-3.18707500
C	6.71121500	-5.10447100	1.00902000
H	5.99222200	-3.15470300	0.48801700
C	9.11175900	-5.34885900	1.14978300
H	10.26898500	-3.57840900	0.78238800
C	12.71947100	1.23790100	-3.57853500
H	12.91548500	2.93475800	-2.25705600
H	12.26220200	-0.55544200	-4.68324800
C	7.83279000	-5.92035600	1.24430500
H	5.71850000	-5.53768400	1.07212100
H	9.98976900	-5.96164700	1.33738700

C	13.81543300	1.68561100	-4.45644300
C	7.70573700	-7.34899200	1.58366500
H	14.28931800	2.62914000	-4.15509700
N	14.19402400	1.03275500	-5.49364000
H	8.65917100	-7.86972500	1.74395700
N	6.57598700	-7.94780400	1.68548800
H	6.71613300	-8.93052000	1.92686400
H	-14.95742000	5.44463600	-3.13066600
H	14.96429500	1.51852700	-5.95651000
O	4.47642100	5.85056200	2.67388200
H	4.62751000	6.17428000	1.77258500

Sum of electronic and thermal Free Energies = -2726.754796 (Hartree/Particle).

From TDDFT calculation in acetonitrile solvent, λ_{abs} = 515.66 nm.

Table S24: DFT-optimized geometry of **BNAH** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-4.25154900	-0.92349100	-1.08449400
C	-2.92238300	-1.03474600	-1.50350300
C	-1.88474100	-0.56947800	-0.68846400
C	-2.16477200	0.01346300	0.55410200
C	-3.50044700	0.12899500	0.96505700
C	-4.53812200	-0.33911600	0.15451500
H	-5.05678800	-1.28300700	-1.71838600
H	-2.69013500	-1.48152800	-2.46599900
H	-0.85684900	-0.65454300	-1.02724200
H	-3.73012100	0.58970400	1.92300600
H	-5.56787700	-0.24140800	0.48618700
C	-1.05608800	0.49177200	1.48228400
H	-0.84686700	-0.27483300	2.23560900
H	-1.39078400	1.38042700	2.02868000
N	0.20026900	0.80577300	0.80978200
C	1.22377800	-0.10186800	0.74963300
C	0.29521200	1.97406100	0.03368000
C	2.34287700	0.06679400	-0.00840900
H	1.06671100	-0.98969000	1.35296000
C	1.34391700	2.22499100	-0.76237600
H	-0.54069700	2.65664100	0.13702100
C	2.50389500	1.27027900	-0.92616800
H	1.35819400	3.15644400	-1.31955700
H	3.45465400	1.78223700	-0.71629500
C	3.42774100	-0.92417300	-0.03088900
O	4.31370500	-0.87648000	-0.90710000
N	3.44411400	-1.93570600	0.90392200
H	4.27612200	-2.51006400	0.90693900
H	2.99819700	-1.81794000	1.80180900
H	2.59000600	0.94404300	-1.97366700

Sum of electronic and thermal Free Energies = -688.418317 (Hartree/Particle).

Table S25: DFT-optimized geometry of **BNAH**$^{\cdot+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	-4.32314600	-0.79231800	-1.02196700
C	-3.18093400	-1.60231200	-1.01399900
C	-2.10931700	-1.29115300	-0.17592500
C	-2.17103200	-0.16529400	0.65896000
C	-3.31326500	0.64405900	0.64630900
C	-4.38918500	0.32859400	-0.19006700
H	-5.15732900	-1.03653600	-1.67264500
H	-3.12750500	-2.47580800	-1.65648000
H	-1.22567000	-1.92384800	-0.17192600
H	-3.36742100	1.51599400	1.29246200
H	-5.27373300	0.95801500	-0.19046600
C	-1.00145800	0.17580300	1.55764100
H	-0.68875400	-0.67954000	2.15730900
H	-1.24595200	0.99650200	2.23573500
N	0.18232100	0.60340800	0.76001000
C	1.30290300	-0.18364000	0.71434900
C	0.10257900	1.77244900	0.03665800
C	2.38505800	0.15207600	-0.05060400
H	1.25794600	-1.09199700	1.30107800
C	1.13053500	2.17881300	-0.75478300
H	-0.82218600	2.32520300	0.13626800
C	2.37704900	1.38547800	-0.88880500
H	1.03554100	3.10793600	-1.30452700
H	3.25353500	2.01424900	-0.65369500
C	3.57939800	-0.75005400	-0.17320700
O	4.17883300	-0.81110200	-1.25140100
N	3.92421800	-1.47404700	0.91524400
H	4.73809100	-2.07121300	0.85081800
H	3.55982700	-1.28212200	1.83715900
H	2.55206600	1.11144200	-1.94400000

Sum of electronic and thermal Free Energies = -688.230213 (Hartree/Particle).

Table S26: DFT-optimized geometry of **BNA**$^{\cdot}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z

C	-4.31384100	-0.88065500	-1.02425700
C	-3.00130600	-1.19262200	-1.39547400
C	-1.92840000	-0.77738800	-0.60179600
C	-2.15481000	-0.04351300	0.57070900
C	-3.47051800	0.27306700	0.93277300
C	-4.54596900	-0.14645700	0.14314500
H	-5.14707500	-1.20183300	-1.64232700
H	-2.81177000	-1.75744200	-2.30367700
H	-0.91249400	-1.01700400	-0.90197300
H	-3.65660100	0.85186200	1.83419400
H	-5.56087000	0.10726500	0.43539100
C	-1.00242900	0.37640500	1.47078900
H	-0.75523200	-0.43042100	2.16744600
H	-1.29866500	1.24088200	2.07568700
N	0.21607300	0.71976800	0.73948200
C	1.29403900	-0.11976900	0.71852700
C	0.22443800	1.89139600	-0.05108000
C	2.40898100	0.13366900	-0.04494800
H	1.18960400	-1.01339500	1.32265100
C	1.32039600	2.16611900	-0.84342000
H	-0.66098200	2.50825700	0.00906700
C	2.43216700	1.31577400	-0.88275300
H	1.30016200	3.07014200	-1.44483000
C	3.55738100	-0.80150300	-0.07535100
O	4.37605300	-0.78208400	-1.01184300
N	3.68454700	-1.71300200	0.94196700
H	4.52148800	-2.27968400	0.93294600
H	3.26722200	-1.55229500	1.84668100
H	3.29167600	1.51583600	-1.50784400

Sum of electronic and thermal Free Energies = -687.808373 (Hartree/Particle).

Table S27: DFT-optimized geometry of **CO_2** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16926700
O	0.00000000	0.00000000	-1.16926700

Sum of electronic and thermal Free Energies = -188.602657 (Hartree/Particle).

Table S28: DFT-optimized geometry of **CO** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

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

Sum of electronic and thermal Free Energies = -113.332229 (Hartree/Particle).

Table S29: DFT-optimized geometry of **H_2O** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
O	0.00000000	0.00000000	0.11771800
H	0.00000000	0.76688300	-0.47087200
H	0.00000000	-0.76688300	-0.47087200

Sum of electronic and thermal Free Energies = -76.438564 (Hartree/Particle).

Table S30: DFT-optimized geometry of **CH_4** (singlet), computed at the B3LYP-D3/ 6-31+G** level in acetonitrile solvent using PCM.

Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
H	0.63111500	0.63111500	0.63111500
H	-0.63111500	-0.63111500	0.63111500
H	-0.63111500	0.63111500	-0.63111500
H	0.63111500	-0.63111500	-0.63111500

Sum of electronic and thermal Free Energies = -40.499246 (Hartree/Particle).

Table S31: Fractional atomic coordinates for the unit cell of AA stacked **TFPB-TRZ** COF.

Space group: P31m

Unit cell parameter: a = b = 35.60 Å, c = 3.49 Å

α = β = 90°, γ = 120°

Atoms	**x/a**	**y/b**	**z/c**
C	-0.28819	0.36675	-1.07067

C	-0.29688	0.32359	-1.07123
H	-0.27022	0.3175	-1.07097
C	-0.24232	0.40408	-1.06607
C	-0.20758	0.39917	-1.20085
C	-0.23245	0.44523	-0.92484
C	-0.16487	0.43355	-1.18625
H	-0.21292	0.36924	-1.32834
C	-0.18989	0.47992	-0.92288
H	-0.25706	0.45089	-0.80253
C	-0.15569	0.47432	-1.04899
H	-0.13914	0.42842	-1.29097
H	-0.18352	0.51097	-0.81131
C	-0.11088	0.51116	-1.03098
H	-0.10565	0.54264	-0.94334
N	-0.07807	0.50597	-1.10711
C	-0.03394	0.54028	-1.08686
N	-0.02148	0.58186	-1.00192
N	0	0.53428	-1.14299
H	0	0.50567	-1.20869

Table S32: Fractional atomic coordinates for the unit cell of AB stacked **TFPB-TRZ** COF.

Space group: P31c

Unit cell parameter: a = b = 35.41 Å, c = 6.95 Å

$\alpha = \beta = 90°$, $\gamma = 120°$

Atoms	x/a	y/b	z/c
C	1.04378	1.03566	0.0816
C	1.03475	0.99209	0.08069
H	1.06135	0.98607	0.08103
C	1.09038	1.07354	0.08973
C	1.12659	1.06747	0.05936
C	1.09978	1.11661	0.13021
C	1.16941	1.102	0.0769
H	1.12305	1.03661	0.0171
C	1.14261	1.15106	0.1454
H	1.07485	1.12486	0.15643
C	1.17775	1.14403	0.12205
H	1.19601	1.09569	0.05418
H	1.14824	1.18337	0.17869
C	1.22259	1.18081	0.14737
H	1.22714	1.21206	0.19364
N	1.25613	1.17598	0.11774
C	1.30024	1.21002	0.14664
N	1.31186	1.24948	0.22173
C	0.70164	1.37678	0.20316
C	0.65828	1.36796	0.20285
H	0.65178	1.39477	0.20375
C	0.73845	1.42255	0.20724
C	0.73671	1.45523	0.09916
C	0.77551	1.43403	0.32094
C	0.77102	1.49838	0.10591
H	0.70899	1.44739	0.00778
C	0.80993	1.47708	0.32641

H	0.77763	1.40985	0.40837
C	0.80794	1.50967	0.21998
H	0.76872	1.52279	0.02105
H	0.83799	1.48504	0.4159
C	0.84453	1.55501	0.2307
H	0.874	1.5614	0.30563
N	0.84127	1.58701	0.15758
C	0.87548	1.6316	0.16596
N	0.91593	1.64502	0.23387
N	0.3349	1.20533	0.10967
H	0.33559	1.17827	0.05438

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