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Supporting Information

Metal Free 3D Donor-Acceptor COF with Low Exciton Binding for Solar Fuel Production Based on CO_2 Reduction

Anupam Dey[a], Faruk Ahamed Rahimi[a], Soumitra Barman[a], Arpan Hazra[a], Tapas Kumar Maji[a]*

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

*E-mail: tmaji@jncasr.ac.in

2. Experimental section.

2.1 Materials: All the chemicals and solvents were purchased from commercial sources and used without purification. Tetrakis(triphenylphosphine)palladium (0) (99%) was purchased from Sigma–Aldrich. 1,1,2,2-Tetraphenylethylene (98%) and Tris(p-aminophenyl) amine were purchased from Alfa Aesar. Bromine (99.99%), 1,4-Dioxane, n-butanol (99.5%), o-dichlorobenzene (99%), acetic acid (99.8%), aniline and 4-formylphenylboronic acid (95.0%) were purchased Spectrochem.

2.2 Characterization techniques and instrumentation:

- **NMR (Liquid State):** ^{1}H NMR and ^{13}C NMR spectrum were recorded on Bruker AVANCE-400 spectrometer (at 400 MHz) with chemical shifts recorded as ppm, and all spectra were calibrated against TMS.
- **PXRD:** X-ray diffraction patterns for COF was recorded in Rigaku Smart Lab SE instrument using Cu-Kα radiation (λ = 1.5406 A^{o}).
- **TGA:** 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.
- **N_2 Sorption isotherm:** N_2 adsorption measurements were carried out at 77 K in a QUANTACHROME QUADRASORD-SI analyzer. Samples were degassed at 150 °C and 1×10^{-1} Pa vacuum for 12 h before performing adsorption isotherm measurement.
- **FTIR:** FTIR spectra were recorded in Bruker FT-IR spectrometer. Samples were prepared as pellets using KBr for IR measurement.
- **^{13}C-Solid State NMR:** ^{13}C-Solid state cross-polarization magnetic angle spinning (CP/MAS) NMR spectrum measured on a Varian infinity plus 300WB spectrometer.
- **FESEM, EDS and TEM analysis:** 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. Energy dispersive spectroscopy (EDS) analysis was performed with an EDAX genesis instrument attached to the FESEM column. Transmission Electron Microscopy (TEM) analysis has been performed using JEOL JEM-3010 with an accelerating voltage at 300 kV.

- **Solid State UV-Vis Study:** Solid state UV-Vis studies were performed in solid state using Perkin Elmer Model Lambda 900 spectrophotometer instrument.

- **Temperature Dependent Photoluminescence (TDPL):** The temperature dependent photoluminescence (TDPL) studies were performed on an Edinburgh instrument (FLS 1000) by coated the sample on a quartz plate. In the range of 125-400K photoluminescence (PL) spectra have been recorded and from these integrated PL data E_b was calculated by using the Arrhenius equation, $I_T = I_0 /(1 + A\ exp(-E_b / k_BT));$ where I_0 = initial integrated PL data at 125K, I_T = integrated PL data at different temperature, A = pre-exponential factor, E_b = exciton binding energy, k_B = Boltzmann constant (8.6173×10^{-5} eVK^{-1}) and T = temperature in kelvin scale.

We have plotted, $ln\ [(I_T/I_0)-1]$ against $1/kT$ and fitted the data following linear equation $Y=a+b*X$. From slope we have calculated exciton binding energy, E_b = 84.2 meV.

- **Time-Resolved Photoluminescence (TRPL):** The time-resolved photoluminescence (TRPL) study was also performed on an Edinburgh instrument (FLS 1000) in MeCN dispersed medium. Lifetime data for TT-COF in Ar, CO_2 purged atmosphere and TEA added CO_2 atmosphere were collected upon exciting at 510 nm. The average lifetime is calculated using following formula-

$$\tau_{avg} = \Sigma a_i \tau_i$$

Where, τ_{avg} = average lifetime in nanoseconds, a_i = Normalized pre-exponential factor of the i-th components that exist in the excited state, τ_i = sum of excited-state lifetime of i-th component. The details are provided in **Table S3**.

- **Electrochemical Characterization:** The electrochemical experiments i.e., Mott-Schottky analysis, impedance measurement and transient photocurrent measurement were carried out with a portable CHI760E workstation (CHI Instruments, USA) via a conventional three-electrode system in a N_2 purged 0.2 M Na_2SO_4 aqueous solution. The Ag/AgCl electrode and platinum plate were used as the reference electrode and counter electrode respectively. For preparation of working electrode, 5 mg of TT-COF was dispersed in a solution of 100 µL water, 100 µL isopropyl alcohol (IPA) and 10 µL of nafion and kept it for sonication upto 30 min to prepare homogenous ink.

(i) **Mott-Schottky Analysis:** For electrode preparation, 12 µL of the slurry coated on glassy carbon electrode and then dried in room temperature and it was done at 4 different frequencies (at 2000 Hz, 3000Hz, 4000Hz and 5000Hz) in the potential window of −2.0 to +2.0 V.

(ii) **Electrochemical Impedance Measurement:** For electrode preparation, 12 µL of the slurry coated on glassy carbon electrode and then dried in room temperature and a white LED lamp (LEICA KL1600 LED) was used for illumination and measurement was recorded at −1.4 V (vs Ag/AgCl) applied bias from 0.1 Hz to 100 kHz (under the dark condition and LED lamp).

(iii) **Transient Photocurrent Measurement:** For electrode preparation, 300 µL of same slurry coated on ITO glass plate (1 cm x 1 cm) and then dried in room temperature. The transient photocurrent responses were carried out in presence of 290 W Xenon arc lamp upon consecutive light "ON-OFF" cycles for 30 s over 16 cycles.

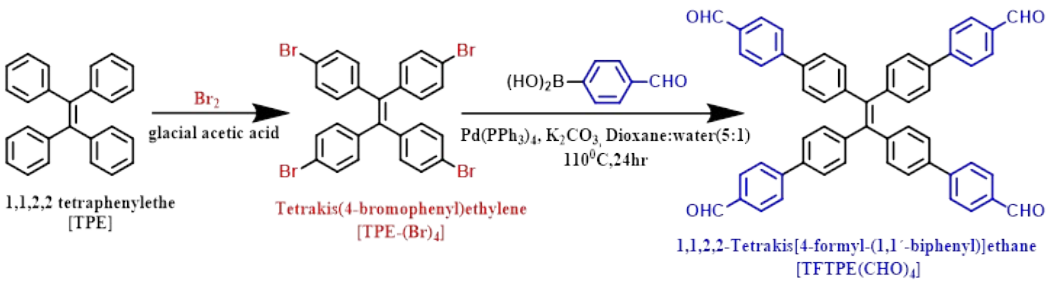
2.2 Synthesis:

A. Synthesis of Tetrakis(4-bromophenyl) ethylene [TPE-$(Br)_4$]:

To an ice-water bath solution of 1, 1, 2, 2-Tetraphenylethylene (TPE, 5, 6.64 g, 20 mmol) in 40 mL glacial acetic acid, Bromine (8.3 mL, 160 mmol) was added dropwise via a pressure-equalizing dropping funnel in 15 minutes, under Argon atmosphere. After further adding 30 mL dichloromethane (DCM), the solution was heated to 50 ^{o} C for 30 minutes. The reaction mixture was then carefully poured into 200 mL ice water, and the resulted precipitate was filtered and washed with 50 mL water and 50 mL ethanol, three times, respectively. After dried at 100 ^{o} C under vacuum overnight, the obtained product tetra (4-bromophenyl) ethylene **[TPE-(Br)$_4$]** was used directly for the next step without further purification.

B. Synthesis of 1,1,2,2-Tetrakis[4-formyl-(1,1´-biphenyl)]ethane [TFTPE(CHO)$_4$]:

TFTPE (CHO)$_4$ was synthesized according to a published procedure.[1] An aqueous solution of K_2CO_3 (1.66 g, 12 mmol) in water (15 mL) and tetrabutylammonium bromide (1.13 g) were added to a solution of tetrakis(4-bromophenyl)ethylene (684 mg, 1.00 mmol) and 4-formylphenylboronic acid (900 mg, 6.00 mmol) in toluene (80 mL). Pd (PPh_3)$_4$ (10 mg, 10 mole %) was added, and then the mixture was stirred at 85 °C for 24 h. After cooling to room temperature, water was added, and the organic layer was separated in $CHCl_3$. Further, purification was carried out by column chromatography in $CHCl_3$/Acetone (95/5) solvent mixture. Then recrystallization in $CHCl_3$/diethyl ether gave a yellowish-green solid (535 mg, 71%); **^{1}H-NMR (DMSO-d$_6$, 25 °C, 400 MHz):** δ (ppm) = 10.03 (s, 4H), 7.94 (d, J = 8.3 Hz, 8H), 7.91 (d, J = 8.3 Hz, 8H), 7.69 (d, J = 8.3 Hz, 8H), 7.24 (d, J = 8.3 Hz, 8H). **^{13}C-NMR (DMSO-d$_6$, 25 °C, 400 MHz):** δ (ppm)= 192.68, 144.91, 143.33, 140.35, 136.89, 135.07, 131.66, 130.12, 127.08, 126.70. **MALDI:** m/z=748.066 (molecular mass).



Scheme-S1. Synthesis of TFTPE $(CHO)_4$

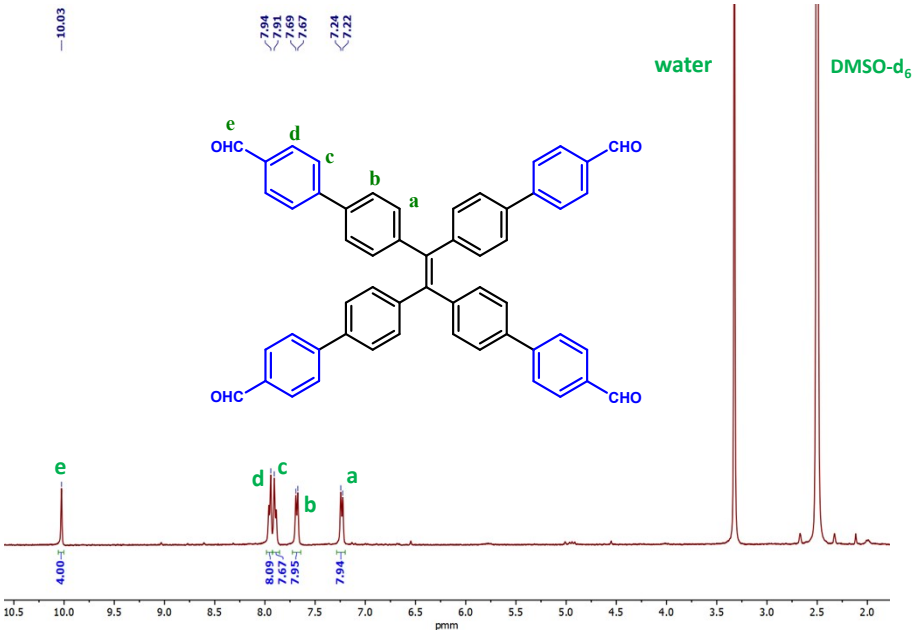


Fig. S1. ^{1}H-NMR of TFTPE $(CHO)_4$

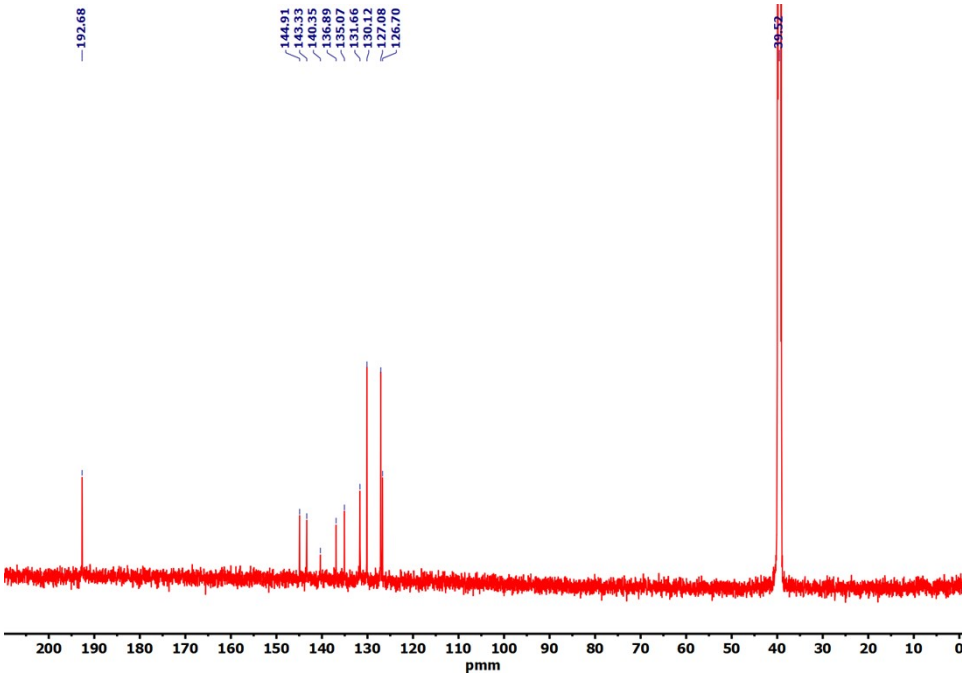
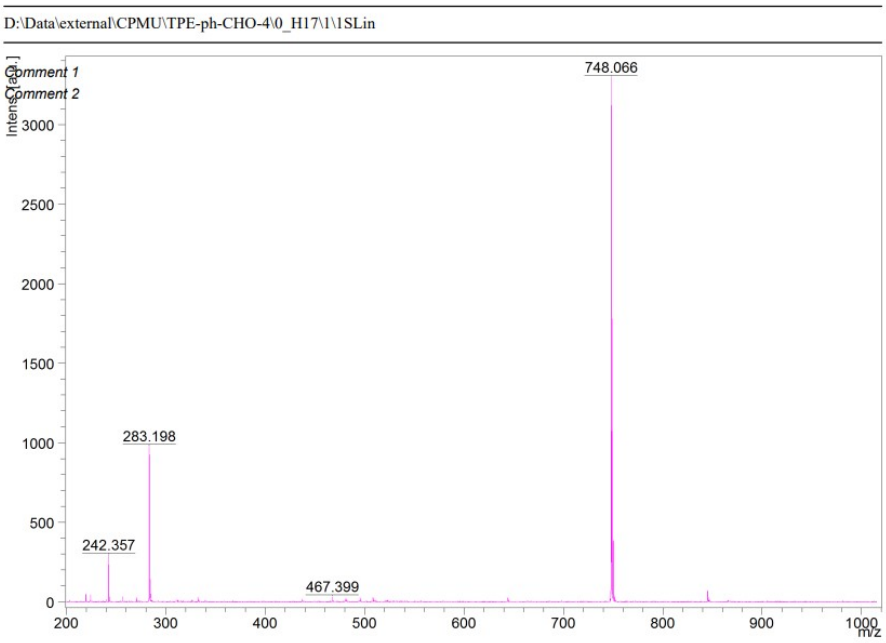


Fig. S2. ^{13}C-NMR of TFTPE (CHO) $_4$



m/z	S/N	Quality Fac.	Res.	Intens.	Area
242.357	37		1561	294	57.6
256.344	4		2046	33.0	11.1
283.198	122		2780	978	280
467.399	4		3239	33.0	12.9
495.373	4		3488	28.0	13.6
748.066	468		628	3298	1992

Fig. S3. MALDI of TFTPE (CHO) $_4$

Synthesis of TT-COF:

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was loaded with TFTPE(CHO)$_4$ (11.2 mg, 0.015 mmol), tris(4-aminophenyl) amine (TAPA) (5.8 mg, 0.02 mmol), n-BuOH (0.5 mL) and o-dichlorobenzene (O-DCB) (0.5mL) and sonicated for 15 mins. After 0.1 mL aqueous acetic acid (6 M) and aniline (27 uL, 0.21 mmol) addition the mixture was again sonicated for 10 mins 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 an orange solid, COF-19. The solid was isolated by filtration and washed with dry THF and dried at 60 °C for 3 h to yield 14.1 mg TT-COF (82% yield based on TFTPE(CHO)$_4$).

Table S1. Fractional atomic coordinates for the unit cell of TT-COF.

TT-COF **Space group:** C2/M **a** = 47.318491 Å, **b** = 90.970425 Å, **c** = 28.01194Å **α**= 90º, **β** = 88.30852º, **γ** = 90º							
Atoms	X	Y	Z	**Atoms**	X	Y	Z
C1	0.61607	0.73547	-0.07746	**C103**	1.08278	0.79148	0.61116
C2	0.09241	0.24089	-0.05192	**C104**	1.10009	0.79947	0.64131
C3	0.08181	0.23336	-0.01179	**C105**	1.10839	0.79346	0.68419
C4	0.59478	0.7203	0.00296	**C106**	1.07351	0.79786	0.56651
C5	0.61778	0.71459	-0.02409	**C107**	1.06003	0.7947	1.05146
C6	0.62835	0.72217	-0.06413	**C108**	1.05125	0.80105	1.09471
C7	0.58549	0.71325	0.04818	**C109**	1.06787	0.79954	1.1345
N8	0.57372	0.68406	0.19893	**C110**	1.09307	0.79157	1.13192

C9	0.56784	0.67859	0.2458	**C111**	1.10188	0.78516	1.08886
C10	0.05365	0.18735	0.28024	**C112**	1.05847	0.80594	1.1793
C11	0.04871	0.18212	0.32611	**C113**	0.20345	0.72075	0.68894
C12	0.55765	0.66802	0.338	**C114**	0.2118	0.7143	0.64626
C13	0.57245	0.65935	0.30422	**C115**	0.20265	0.70024	0.63556
C14	0.57788	0.66471	0.25831	**C116**	0.18484	0.69254	0.66717
C15	0.35662	0.4862	0.39782	**C117**	0.17674	0.69882	0.7105
C16	0.85236	0.97915	0.4419	**C118**	0.21194	0.69395	0.5907
C17	0.83853	0.96553	0.44426	**C119**	0.16343	0.70657	0.08823
C18	0.82889	0.95886	0.40221	**C120**	0.17182	0.70055	0.13106
C19	0.3324	0.46645	0.35862	**C121**	0.18962	0.70843	0.1607
C20	0.34624	0.47991	0.35646	**C122**	0.19892	0.72238	0.14726
C21	0.81607	0.94394	0.40256	**C123**	0.19033	0.72855	0.10479
N22	0.2804	0.39123	0.41477	**C124**	0.19907	0.70207	0.20529
C23	0.26708	0.37775	0.40308	**H125**	0.08262	0.25106	-0.06272
C24	0.27607	0.36556	0.42762	**H126**	0.06402	0.23788	0.00845
C25	0.26374	0.35207	0.41982	**H127**	0.62773	0.7044	-0.01401
C26	0.24193	0.3507	0.38731	**H128**	0.64648	0.71791	-0.08409
C27	0.73402	0.86272	0.35979	**H129**	0.04662	0.19833	0.27208
C28	0.74644	0.87627	0.3675	**H130**	0.03746	0.18892	0.35207
C29	0.1437	0.25616	-0.11021	**H131**	0.57955	0.64844	0.31377
C30	0.14961	0.26134	-0.06207	**H132**	0.58951	0.65799	0.23249
C31	0.67165	0.75511	-0.03715	**H133**	0.86017	0.9841	0.47404
C32	0.67874	0.76076	0.00698	**H134**	0.83607	0.96015	0.47863
C33	0.16377	0.27276	0.02752	**H135**	0.32448	0.46197	0.32594

C34	0.14087	0.27859	0.00223	**H136**	0.34915	0.48534	0.32235
C35	0.13396	0.27289	-0.04203	**H137**	0.29253	0.36673	0.4533
C36	0.17243	0.27924	0.07408	**H138**	0.27055	0.34281	0.44055
N37	0.18776	0.30999	0.2211	**H139**	0.71759	0.86176	0.33384
C38	0.19731	0.31715	0.26248	**H140**	0.73918	0.8852	0.34565
C39	0.72434	0.82339	0.26256	**H141**	0.68378	0.74606	-0.05222
C40	0.73353	0.8304	0.30343	**H142**	0.6966	0.75582	0.02362
C41	0.21575	0.33107	0.34443	**H143**	0.12802	0.28755	0.01575
C42	0.18843	0.32507	0.34349	**H144**	0.11642	0.27751	-0.06077
C43	0.17919	0.31826	0.30249	**H145**	0.7381	0.82284	0.23097
N44	0.54983	0.66203	0.3836	**H146**	0.75458	0.83509	0.30352
C45	0.15594	0.73538	0.84985	**H147**	0.17438	0.32571	0.37466
C46	0.67907	0.24091	0.82365	**H148**	0.15819	0.31359	0.30225
C47	0.68948	0.23342	0.78375	**H149**	0.68887	0.25115	0.83359
C48	0.17666	0.72025	0.76855	**H150**	0.70748	0.23825	0.7654
C49	0.15426	0.7144	0.79737	**H151**	0.14364	0.70428	0.78922
C50	0.14408	0.72194	0.83747	**H152**	0.12633	0.7175	0.85792
C51	0.18591	0.71312	0.72252	**H153**	0.72401	0.19881	0.49848
N52	0.19755	0.68364	0.57115	**H154**	0.73524	0.18956	0.41942
C53	0.20391	0.67857	0.52414	**H155**	0.19549	0.64828	0.45613
C54	0.71793	0.18767	0.49032	**H156**	0.18364	0.65767	0.5369
C55	0.72412	0.18252	0.44484	**H157**	-0.08694	0.98412	0.30198
C56	0.21653	0.66823	0.43275	**H158**	-0.06255	0.9601	0.29724
C57	0.20172	0.6593	0.46583	**H159**	0.44855	0.46135	0.4496
C58	0.19512	0.66455	0.51138	**H160**	0.42414	0.48521	0.45365

C59	0.41669	0.48614	0.37824	**H161**	0.48088	0.36676	0.32126
C60	-0.07912	0.97912	0.33406	**H162**	0.50388	0.34303	0.33218
C61	-0.0653	0.96548	0.33155	**H163**	0.0577	0.86211	0.43743
C62	-0.05569	0.95881	0.37345	**H164**	0.035	0.88535	0.42761
C63	0.44081	0.46618	0.41724	**H165**	0.08909	0.74565	0.82342
C64	0.42708	0.47975	0.41958	**H166**	0.07613	0.75548	0.7477
C65	-0.04287	0.94402	0.3724	**H167**	0.64362	0.28778	0.75694
N66	0.49245	0.3912	0.3606	**H168**	0.65527	0.27772	0.83338
C67	0.50662	0.37785	0.37091	**H169**	0.03758	0.82458	0.54153
C68	0.49779	0.36567	0.34615	**H170**	0.02191	0.83712	0.46919
C69	0.51072	0.35229	0.35287	**H171**	0.59884	0.32366	0.39456
C70	0.53309	0.35102	0.38434	**H172**	0.61425	0.31122	0.46692
C71	0.04091	0.863	0.41211	**H173**	0.91903	1.06716	0.39798
C72	0.0278	0.87645	0.4056	**H174**	0.94108	1.09172	0.39901
C73	0.62845	0.25608	0.88243	**H175**	1.02029	1.07315	0.35129
C74	0.62264	0.26124	0.83409	**H176**	0.99912	1.04854	0.3497
C75	0.10096	0.75484	0.80869	**H177**	1.01175	1.09631	0.41143
C76	0.09379	0.76052	0.76461	**H178**	1.16698	1.0621	0.66834
C77	0.60844	0.27269	0.74447	**H179**	1.18886	1.08613	0.66936
C78	0.63104	0.27867	0.77014	**H180**	1.22615	1.07894	0.52977
C79	0.63798	0.27296	0.81438	**H181**	1.20497	1.0543	0.52741
C80	0.59982	0.27916	0.69789	**H182**	1.23929	1.09619	0.63524
N81	0.58577	0.30959	0.54993	**H183**	1.07525	0.76022	0.67385
C82	0.57665	0.31683	0.50842	**H184**	1.06052	0.77114	0.60106
C83	0.0508	0.8243	0.50927	**H185**	1.10691	0.81048	0.63195

C84	0.04208	0.83149	0.46844	**H186**	1.12116	0.80035	0.70616
C85	0.55914	0.33116	0.4265	**H187**	1.05657	0.79262	0.54755
C86	0.58532	0.32388	0.42645	**H188**	1.04703	0.79611	1.02083
C87	0.59411	0.31686	0.46742	**H189**	1.03183	0.80733	1.09757
N88	0.22541	0.66241	0.38748	**H190**	1.1055	0.79023	1.1635
C89	0.94095	1.06831	0.38665	**H191**	1.12127	0.77886	1.08742
C90	0.95325	1.08224	0.38688	**H192**	1.03909	0.8018	1.1959
C91	0.98179	1.08371	0.37364	**H193**	0.21091	0.73178	0.69393
C92	0.99803	1.07163	0.36013	**H194**	0.22518	0.72035	0.62105
C93	0.98585	1.05776	0.35944	**H195**	0.17764	0.68158	0.6586
C94	0.9967	1.09693	0.38384	**H196**	0.16353	0.69216	0.73376
C95	1.17959	1.06536	0.63736	**H197**	0.23035	0.69878	0.57312
C96	1.19168	1.07917	0.63816	**H198**	0.15025	0.69977	0.06665
C97	1.20819	1.08391	0.59939	**H199**	0.16463	0.68963	0.14079
C98	1.21255	1.07514	0.55911	**H200**	0.2127	0.72856	0.1699
C99	1.20055	1.06115	0.55816	**H201**	0.19788	0.73949	0.0973
C100	1.22509	1.09667	0.60634	**H202**	0.2154	0.70762	0.22487
C101	1.08242	0.77125	0.66668	**C203**	0.3727	0.5	0.39413
C102	1.07388	0.77742	0.62415	**C204**	0.40062	0.5	0.38201

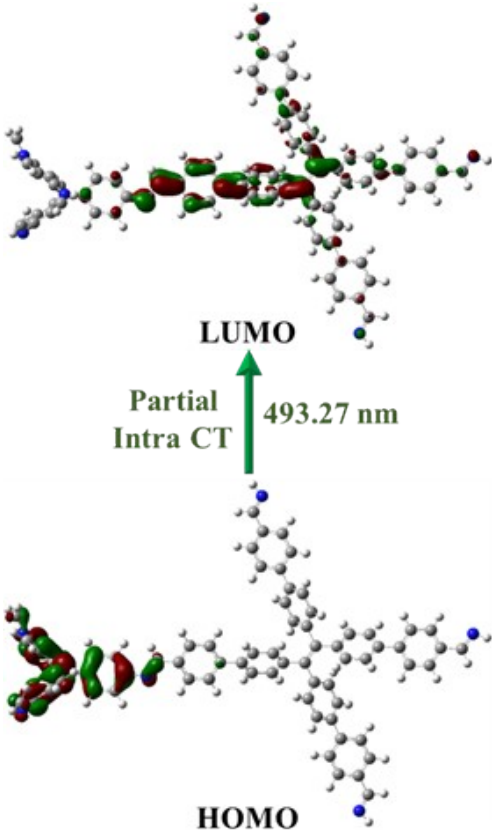


Fig. S4. TDDFT calculation and for **TT-COF**.

Table S2. Assignment of experimental solid-state absorption spectrum of TT-COF.

Absorption maximum	**Transition**	**% Matching**	**Oscillation strength (*f*)**	**Assignment**
490 nm	HOMO→LUMO (493.27 nm)	85% (c = 0.63947)	0.7775	Partial Intra CT

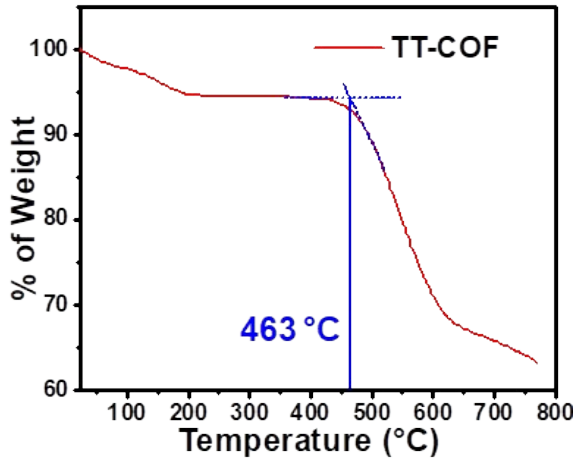


Fig. S5. Thermogravimatric analysis (TGA) of TT-COF under N_2 atmosphere good thermal stability upto 460 °C after some initial weight loss due to trapped solvent molecules inside the framework (boiling point of n-BuOH and O-DCB are 117.7°C and 180.19°C respectively).

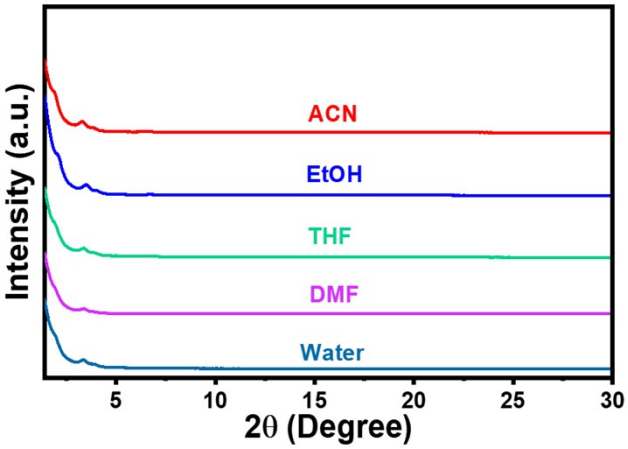


Fig. S6. PXRD patterns of TT-COF after soaking in different solvent for 36 h. After soaked in different solvents at room temperature for 36 h the samples were filtrated, washed with THF and dried in 50 °C for 5 h.

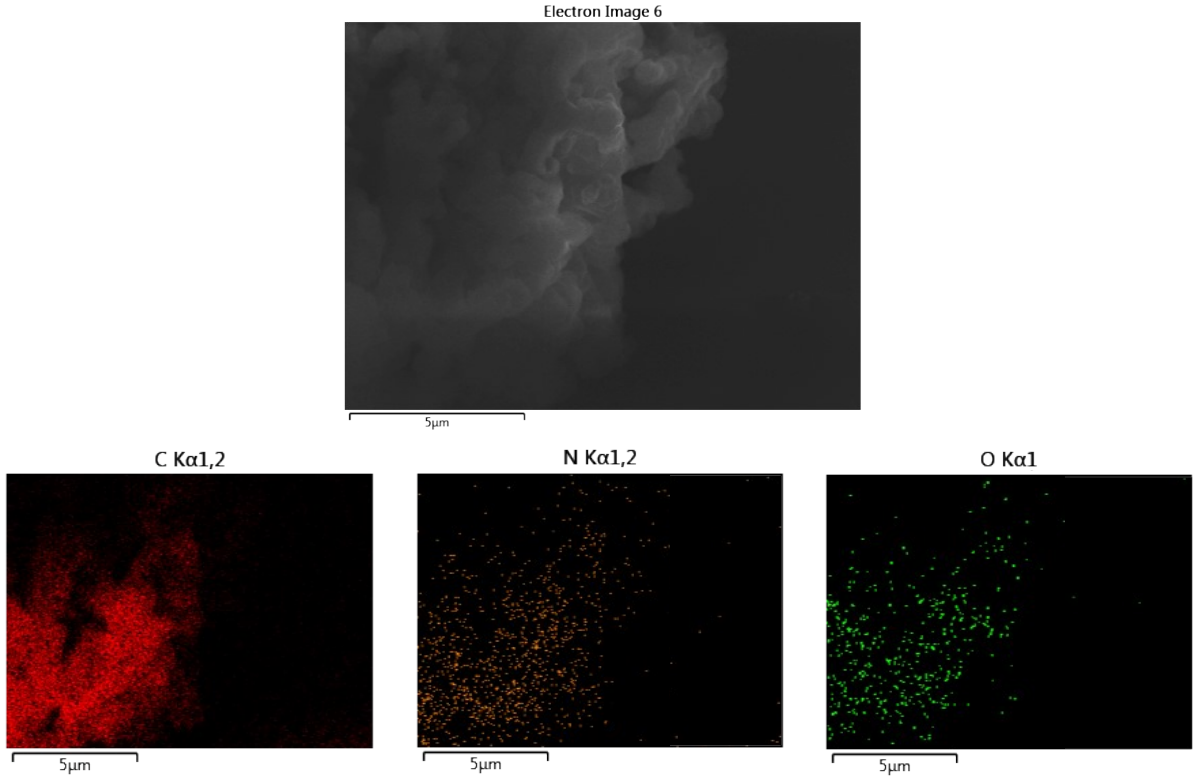


Fig. S7. Elemental mapping for TT-COF displays distribution of C,N and O throughout the framework.

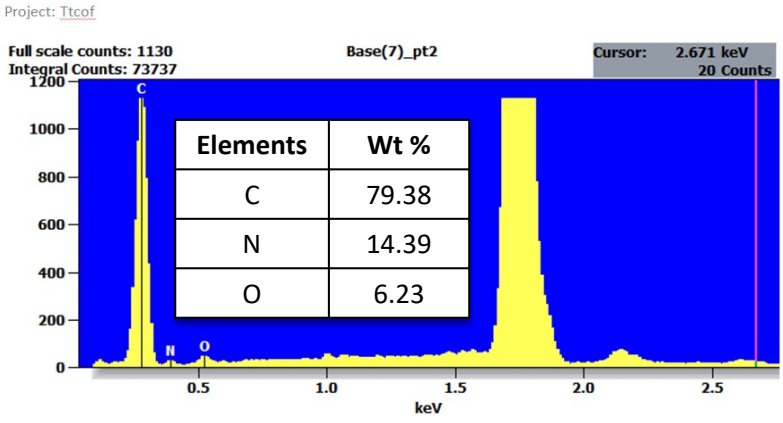


Figure S8. EDAX analysis for TT-COF.

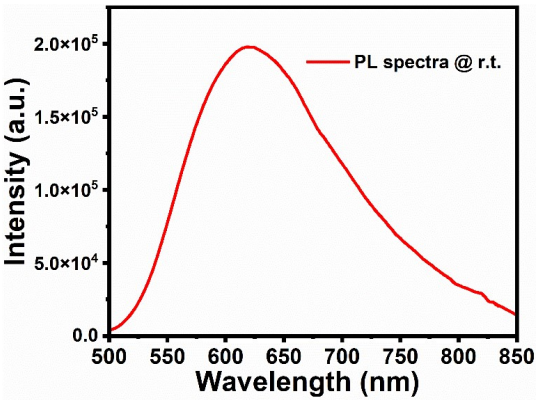


Fig. S9. PL spectrum of TT-COF at room temperature .

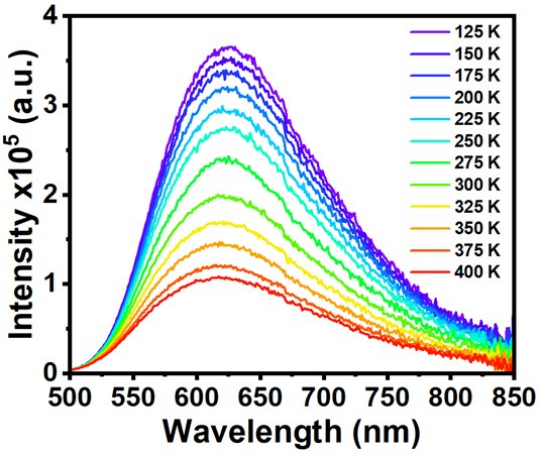


Fig. S10. PL spectra of TT-COF at different temperature.

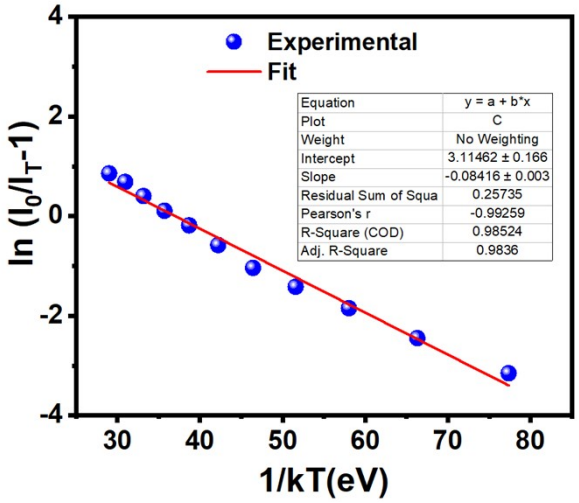


Fig. S11.Plot of *ln [(I_T/I_0)-1]* vs *1/kT* and the data were fitted by linear equation. From slope exciton binding energy, E_b was obtained 84.2 meV which is low.

3. Photocatalytic CO_2 Reduction:

At first, a stock solution was prepared by dispersing 1 mg of finely powdered TT-COF sample in 40 ml MeCN and sonicated for 10 minutes. From this homogeneously dispersed stock solution 5 mL was taken in a 30mL quartz tube vial. Next highly pure CO_2 gas (99.99%) was purged into the reaction mixture for 30 minutes. Then 0.5 mL TEA was added and sealed the setup which makes 24.5 mL of void space. After that, quartz tube vial was kept in front of 290 W Xenon Arc lamp with a visible band pass filter ($\lambda > 420$ nm) with continuous stirring 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 was analysed using gas chromatography mass spectrometry (GC-MS) (SHIMADZU GC-2010 PLUS). Produced gases 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 concentration 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 analysed to determine the amount of liquid product. The liquid product was verified with ^{1}H-NMR using the water suppression method. All controlled photocatalytic experiments were carried out in similar way. Selectivity was calculated by using the following equation:

$$Selectivity\ of\ CO = \frac{2 \times n_{CO}}{(2 \times n_{H_2} + 2 \times n_{CO} + 8 \times n_{CH_4})} \times 100\%$$

- **Isotopic labelling ($^{13}CO_2$) experiment:** For isotopic labelling experiment, 1 L $^{13}CO_2$ gas cylinder was purchased from Sigma Aldrich (details: 99.0% ATOM % ^{13}C, <3 Atom % ^{18}O; M.W. 45.00 g/mol). We have purged the $^{13}CO_2$ for 5 min in a controlled manner to the photocatalytic reaction mixture of TT-COF.

- **Turnover Number (TON) calculation:** The turnover number (TON) is calculated by using the following formula-

$$TON = \frac{Amount\ of\ product\ evolved\ (\mu mol)}{amount\ of\ catalyst\ (\mu mol)}$$

- **Apparent quantum efficiency (AQY):** The apparent quantum efficiency (AQE) is defined by the ratio of the effective electron used for product formation to the total input photon flux. The AQE is calculated by using the below formula.

$$AQE(\%) = \frac{Effective\ elctrons\ in\ product}{Total\ photons} \times 100\% = \frac{n \times Y \times N}{\Theta \times t \times A} \times 100\%$$

Where, n is the number of electrons used in the photocatalysis process, Y is the yield of evolved gas from the sample (mol), N is the Avogadro's number (6.022×10^{23} mol^{-1}), θ is the photon flux, t is the irradiation time, and A is the illumination area. The photon flux was calculated at 400 ± 10 nm, 450 ± 10 nm, 500 ± 10 nm, 550 ± 10 nm, 600 ± 10 nm by using separate bandpass filters with the help of power meter. The power meter (model: LaserCheck: 0623G19R) used for the experiment was purchased from Coherent.

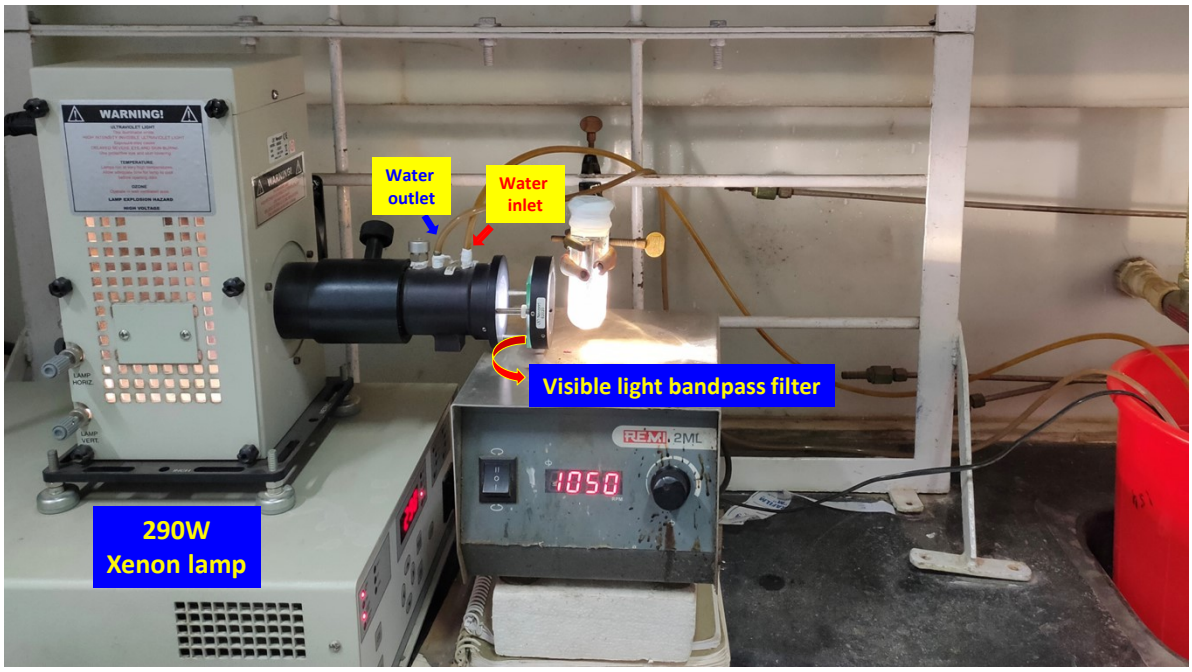


Fig. S12. Photographic image of the photocatalytic CO_2 reduction set up.

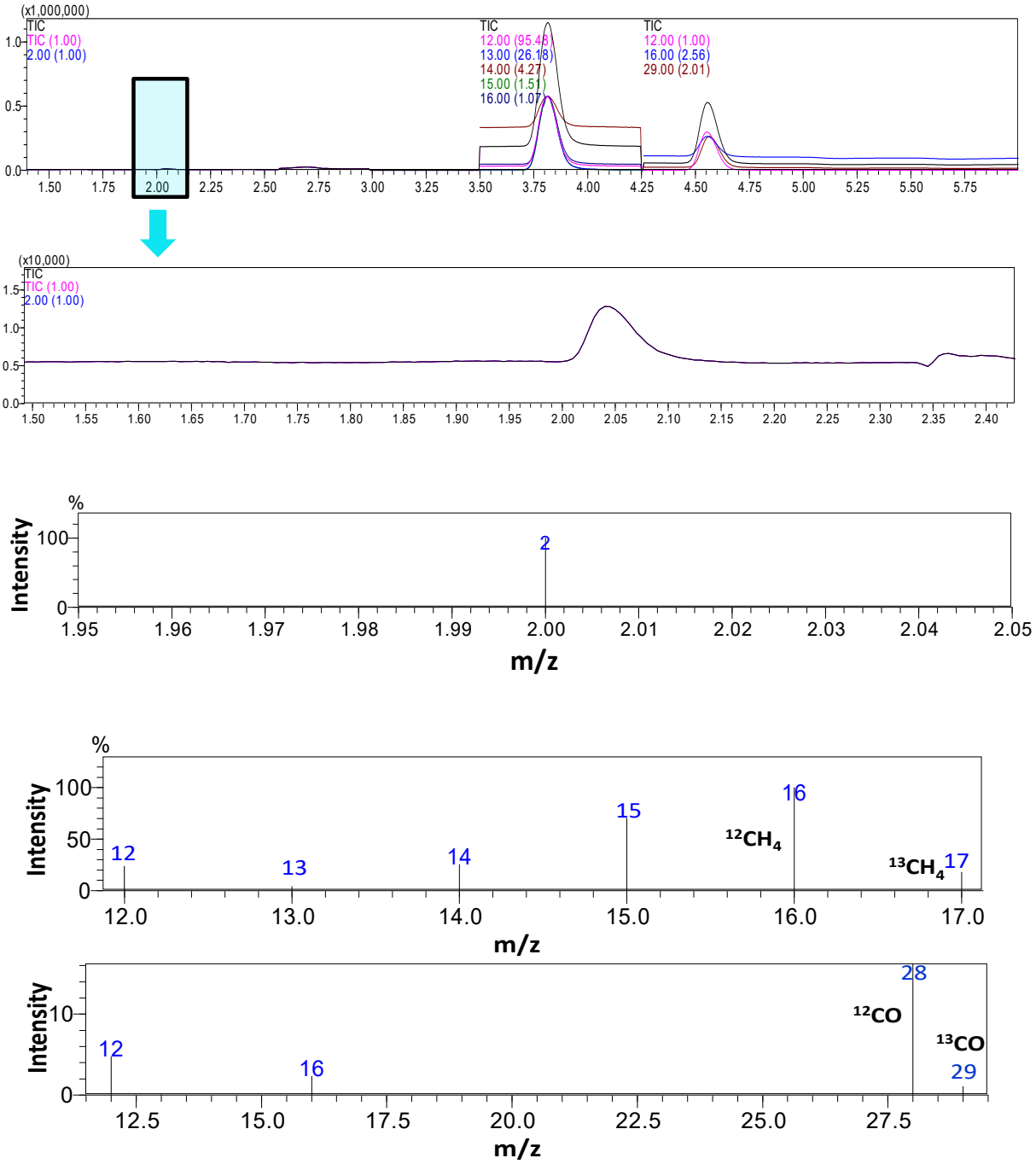


Fig. S13. GC chromatograms and mass spectra of obtained products (CO, CH_4, H_2) from the photocatalytic CO_2 reduction reaction under Xe lamp in $^{12}CO_2$ atmosphere **(a)** GC chromatogram, retention time from 1.4 to 6 min **(b)** Chromatogram part for H_2 detection, retention time from 1.4 to 2.4 min **(b)** Mass spectra for H_2; m/z = 2 is assigned to H_2 **(c)** Mass spectra for $^{12}CH_4$; m/z = 16 is assigned to $^{12}CH_4$. **(d)** Mass spectra for ^{12}CO; m/z = 28 is assigned to ^{12}CO.

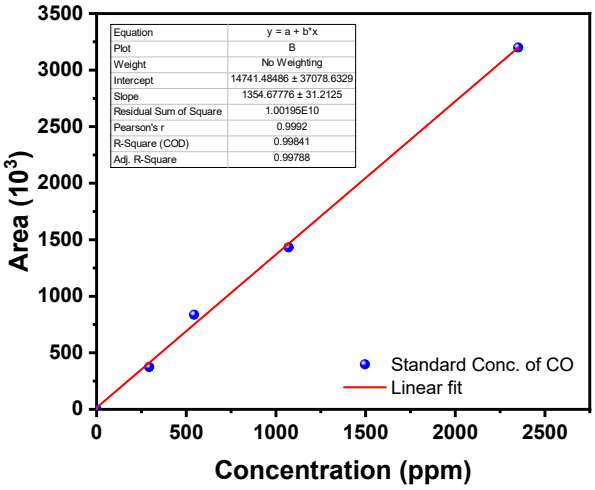


Fig. S14. Calibration plot for CO (calibration was performed by taking different ppm concentrations of CO gas).

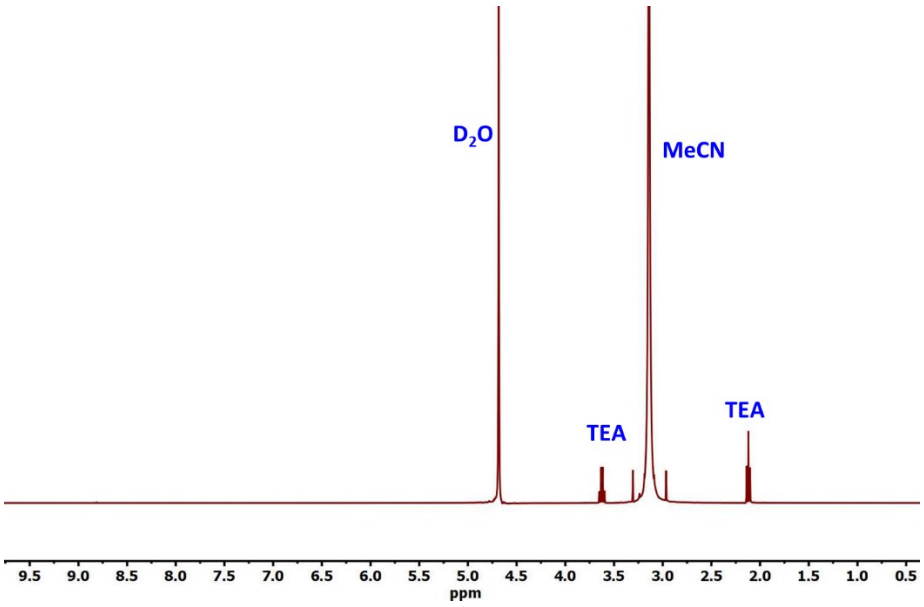
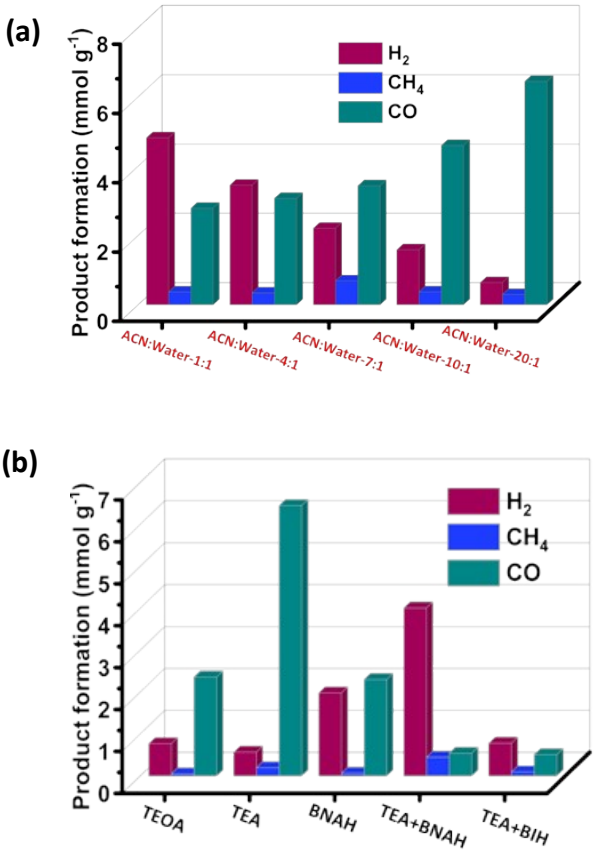


Fig. S15. No liquid product detection in ^{1}H NMR spectrum after 26 h of photoirradtion in presence of CO_2 by TT-COF. After filtration of catalytic reaction mixture, 500 µL of aliquot was taken in the NMR tube with D_2O (50 µL) and 50 µL 4 mM DMSO as an internal standard. Water presaturation method was employed during measurement.



➢ Catalyst a) COF b) Physical mixture of monomers	✓ a -	 x x	✓ a -	✓ a -	✓ - b	✓ a -
➢ Light	x	✓	✓	✓	✓	✓
➢ CO_2	✓	✓	x	✓	✓	✓
➢ TEA	✓	✓	✓	x	✓	✓

Fig. S16. Product distribution after 26 h of photoreduction by TT-COF **(a)** different composition of acetonitrile/water as solvent under CO_2 atmosphere; **(b)** In presence of different sacrificial electron donor under CO_2 atmosphere; **(c)** Controlled catalytic experiments displays the importance of catalyst, light, CO_2 and TEA in the catalysis process.

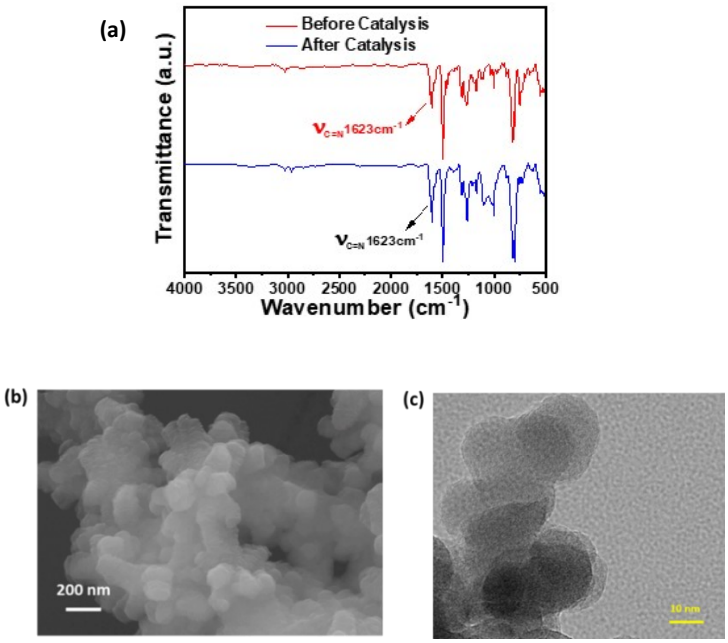


Fig. S17. Chemical and structural stability of TT-COF before and after 26 h irradiation **(a)** FTIR spectra reveals the existence of –C=N stretching band at 1619 cm^{-1} after catalysis as like before catalysis **(b)** FESEM image after catalysis **(c)** HRTEM image after catalysis.

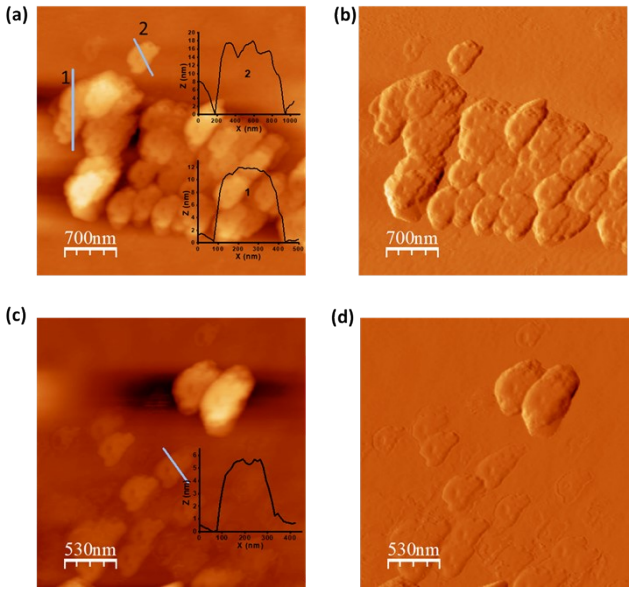


Fig. S18. AFM studies of TT-COF before and after 26 h irradiation **(a) & (b)** Before catalysis AFM images (height and amplitude) of TT-COF having ~12-18 nm height profile; **(c) & (d)**

After catalysis AFM images (height and amplitude) reveal exfoliated sheet kind of morphology having ~6 nm height profile.

Reconversion of TT-COF after Photocatalysis:

After irradiation under visible light for 26 h the TT-COF was filtered washed with MeCN and THF. The organic filtrates were checked for any breakage of monomers from the framework (e.g., $TPETP(CHO)_4$ and TAPA), but no of monomeric species were detected. It was then vacuum-dried, and 15 mg of TT-COF was loaded into a pyrex tube measuring 10 × 8 mm (o.d × i.d). Then n-BuOH (0.5 mL) and o-dichlorobenzene (O-DCB) (0.5mL) were added and sonicated for 5 mins. After 0.1 mL aqueous acetic acid (6 M) and aniline (27 uL, 0.21 mmol) were added and sonicated for 5 mins. Next, 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 and kept to 120 °C for 5 days. The orange solid was isolated by filtration and washed with dry THF and dried at 60 °C for 3 h to recovered TT-COF powder again. It displayed similar PXRD pattern and BET surface area of 707 m^2g^{-1} as earlier case.

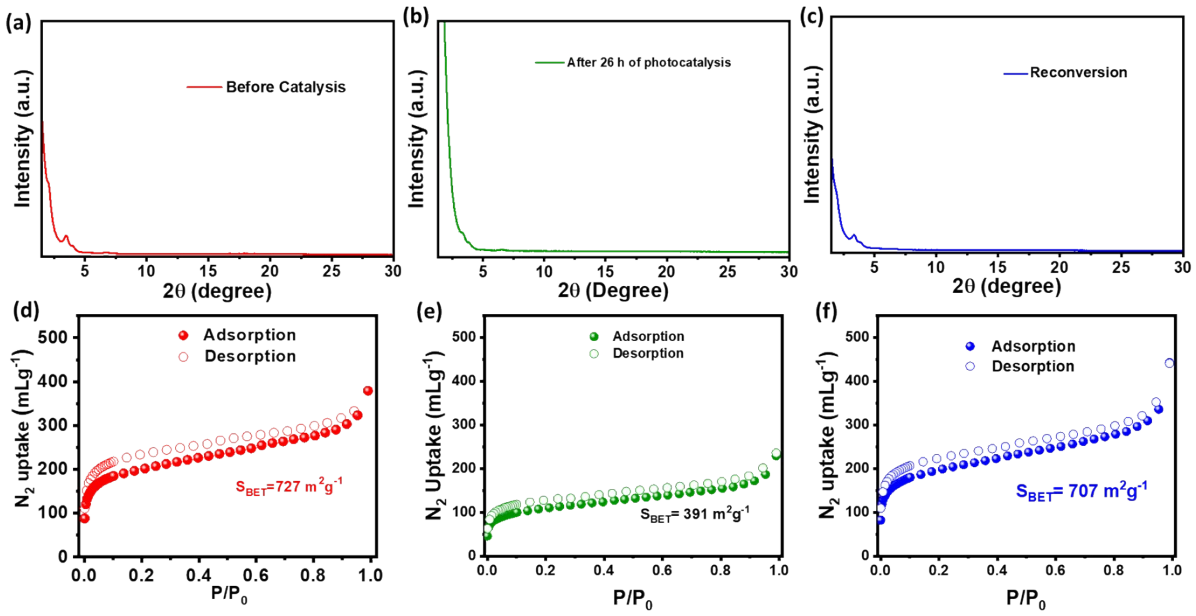


Fig. S19. Experimentally observed powder X-ray diffraction pattern of TT-COF for **(a)** before catalysis- crystalline polymer; **(b)** after 26 h of irradiation-less crystallinity; **(d)** after reconversion- crystalline polymer; BET surface area of TT-COF for **(e)** before catalysis; **(f)** after 26 h of irradiation; **(g)** after reconversion.

- ***In-situ* Diffuse Reflectance FTIR (DRIFT) Measurement:** *In-situ* diffuse reflectance FT-IR measurement was carried out by FT-IR spectrometer (BRUKER Vertex 70V) in the Praying Mentis chamber. One designed reaction cell containing with two ZnSe windows and one quartz window was fixed inside the Praying Mentis chamber. Then the MeCN solution of photocatalyst was drop casted over a glass slide and placed in the center of the designed reaction cell. After these 2 drops of TEA was added on top the sample. Next 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 15 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 64 scan after each 3 min of reaction time.

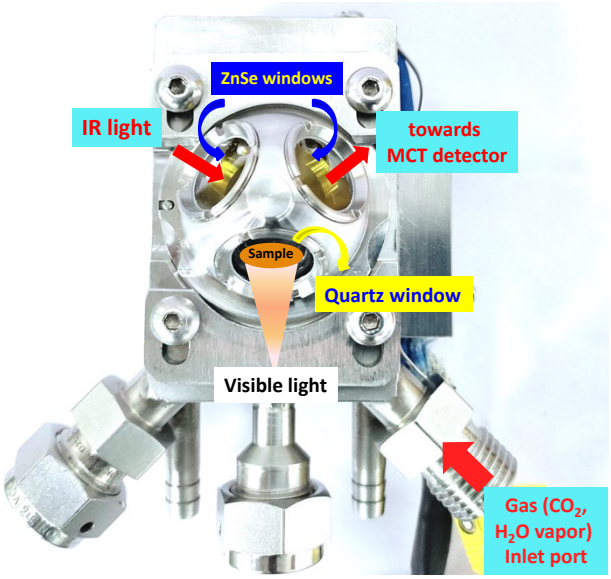


Fig. S20. Photograph of the set-up for *in-situ* DRIFTS.

Table S3.

System	λ_{ex} nm	τ_1 ns	B_1 %	τ_2 ns	B_2 %	τ_3 ns	B_3 %	χ^2	τ_{AVG} ns
TT-COF @ Ar	510	0.377	3.79	3.289	88.69	28.36	7.52	1.122	5.06
TT-COF@ CO_2	510	0.394	25.83	2.996	66.02	14.96	8.14	1.295	3.30
TT-COF@ CO_2-TEA	510	0.321	44.57	1.258	48.68	12.37	7.09	1.289	1.63

COF	Linkage	Light source	Sacrificial agent	Photosensitizer	Product	Yield	Ref.
CTF	Triazine	450 W Xe lamp (λ ≥ 420 nm)	None	Rh[Cp*Rh(bpy) H_2O]$^{2+}$	HCOOH	204.14 μmol	2
CT-COF	Imine	300 W Xe lamp (λ > 420 nm)	None	None	CO	102.7 μmol g^{-1} h^{-1}	3
TFPG-DAAQ COF	Imine	Blue LED light (445 nm)	TEOA	$Co(dmg)_2$	HCOOH	125[a]	4
COF-367 NSs	Imine	300 W Xe lamp (λ > 420 nm)	Ascorbic acid	$Ru(bpy)_3Cl_2$	CO	65 μmol g^{-1} h^{-1}	5
TAPBB-COF	Imine	Xe lamp (200 ≤ λ ≤ 1000 nm)	None	None	CO	24.6 μmol g^{-1} h^{-1}	6

TT-COF	Imine	300 W Xe lamp (λ > 420 nm)	TEA	None	CO	248 μmol g^{-1} h^{-1}	This work

Table S4. Emerging COFs Applied in the Photoreduction of CO_2 as metal-free photocatalyst

[a]TON (calculated using calibration curve of known concentration of HCOOH).

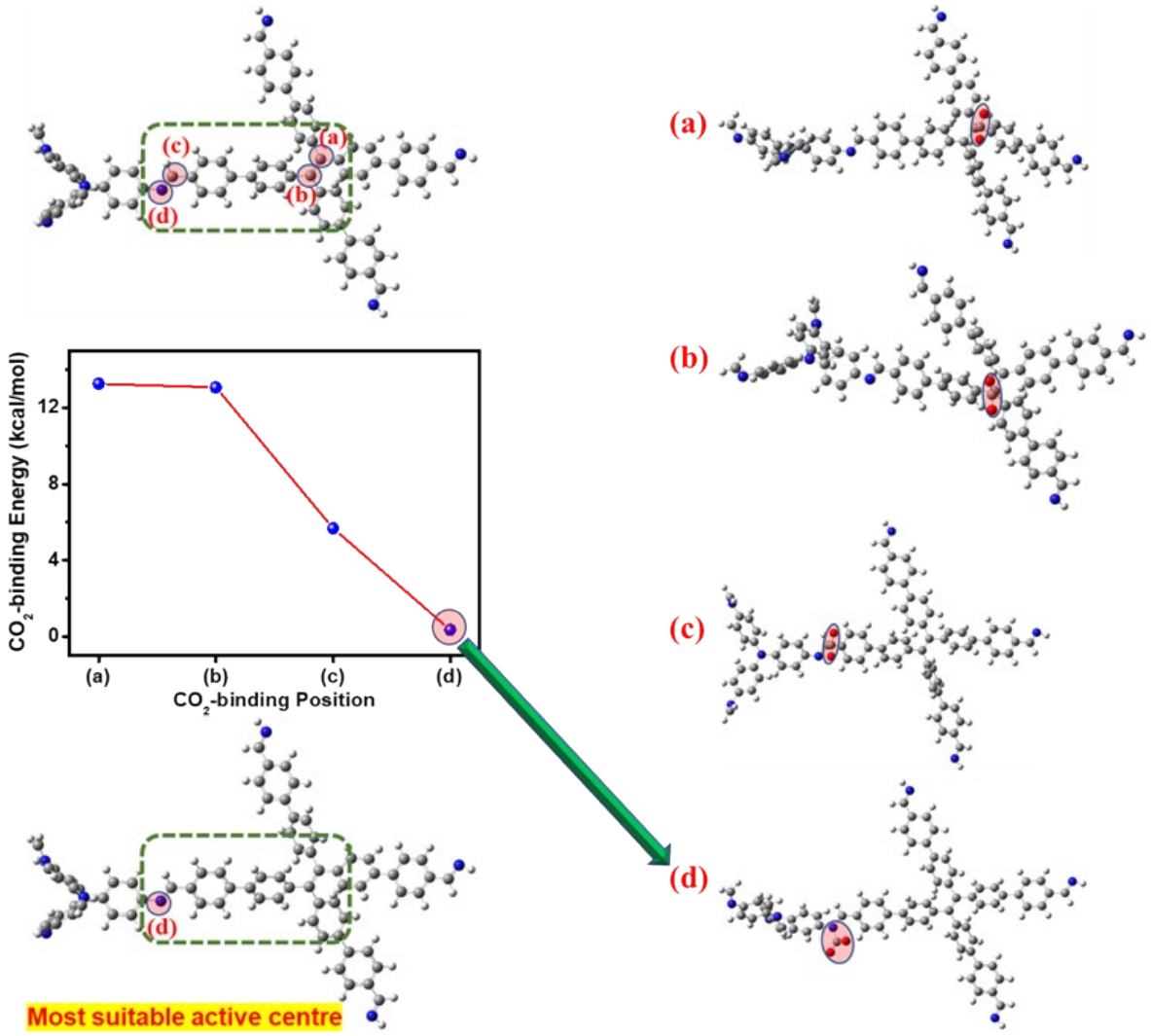


Fig. S21. Identification of the most suitable active centre for CO_2RR by CO_2-binding energy calculations with optimized structures of different CO_2-bound models (model-**a** to model-**d**).

Computational Details:

All the calculations were performed using density functional theory (DFT) in Gaussian16 program package.[7] The geometry optimization and frequency calculations were performed utilizing B3LYP exchange-correlation functional along with 6-31+G* basis set for all atoms.[8-13] The implicit solvent effect of acetonitrile was incorporated into all computations by polarisable continuum model (PCM)[14] Grimme's d3 dispersion was also used to tackle weak interactions.[9] 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). Time-dependent density functional theory (TDDFT) calculations were performed to assess the electronic absorption spectrum. For TDDFT calculations, the same level of theory to that of optimization and frequency calculations, was used. 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. 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.[15]

In **Fig. S16**, all the possible pathways for CO_2 photoreduction to CO on metal-free **TT-COF** catalyst were summarized.

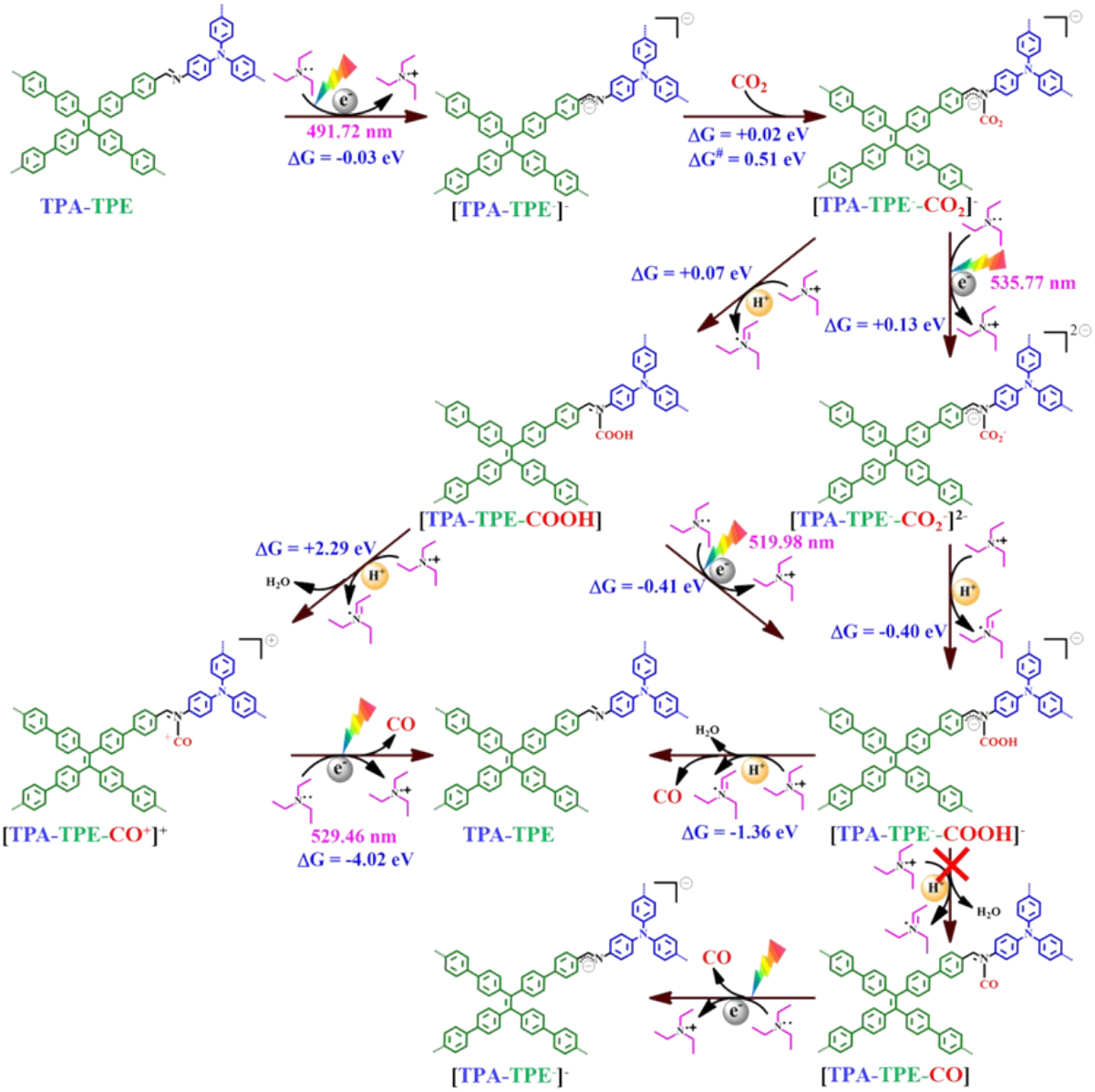


Fig. S22. Complete photocatalytic CO_2-to-CO reduction mechanism with respective relative Gibbs free energy values in acetonitrile solvent and using TEA as the sacrificial electron donor.

Cartesian coordinates of the computed structures

Coordinates are given in standard XYZ format

Table-S5. DFT-optimized geometry of **TPA-TPE** (singlet), computed at the B3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z

N	-11.89753300	-0.88601600	0.05730500
C	-12.60443500	-1.53400400	1.10322100
C	-12.13995300	-1.46893100	2.42736600
C	-13.77137600	-2.26930800	0.83028500
C	-12.82958900	-2.11012400	3.45419400
H	-11.22849400	-0.92212800	2.64914700
C	-14.45652700	-2.91262000	1.85660400
H	-14.13249800	-2.34153200	-0.19100900
C	-14.01087500	-2.82506600	3.18603600
H	-12.43794800	-2.06652500	4.46655600
H	-15.34950500	-3.49154100	1.63707400
C	-12.60797300	-0.20867200	-0.96720500
C	-13.73355600	0.57382600	-0.66005800
C	-12.20881500	-0.32271100	-2.31058500
C	-14.43479200	1.23511000	-1.66599400
H	-14.06521000	0.65423400	0.37068700
C	-12.91292800	0.33545400	-3.31442600
H	-11.35016800	-0.93685200	-2.56393100
C	-14.02148900	1.14190000	-3.00726200
H	-15.31673300	1.81431000	-1.40747600
H	-12.60817400	0.23166700	-4.35226200
C	-10.47933200	-0.93589800	0.02349600
C	-9.73135900	0.19949400	-0.33028600
C	-9.79732800	-2.12760800	0.32549600
C	-8.34016500	0.15023700	-0.37102100
H	-10.24574100	1.12069600	-0.58715600
C	-8.40762400	-2.17516400	0.28433900
H	-10.36294100	-3.01730800	0.58516800
C	-7.65111500	-1.03449600	-0.04245300
H	-7.78841300	1.03479100	-0.67615000
H	-7.88679900	-3.10251500	0.50711600
N	-6.25086800	-1.16474600	-0.07201600
C	-5.49915100	-0.17243700	0.24963500
C	-4.03643700	-0.22359700	0.18293700
H	-5.92211400	0.77460100	0.61355900
C	-3.34112000	-1.36437800	-0.26366700
C	-3.29182000	0.90185700	0.57851000
C	-1.95236500	-1.37423000	-0.30690800
H	-3.90386200	-2.24251900	-0.56508400
C	-1.89939800	0.89079100	0.53154700
H	-3.80935700	1.79695400	0.91666800
C	-1.19996000	-0.24757300	0.08975200
H	-1.43862200	-2.27499800	-0.63091900

H	-1.35081400	1.78312500	0.81931600
C	0.28145400	-0.26090700	0.04141400
C	0.97166500	-0.92932300	-0.98756400
C	1.04533700	0.39171500	1.02784800
C	2.36413700	-0.93537800	-1.03266100
H	0.41487700	-1.42865200	-1.77573700
C	2.43638900	0.39351200	0.97479000
H	0.54697800	0.88212000	1.85958700
C	3.12425600	-0.25595400	-0.06509100
H	2.87090000	-1.45411400	-1.84219400
H	3.00240000	0.90062300	1.75059500
C	4.61263600	-0.25627900	-0.12415200
C	5.34815100	0.88755100	0.01811700
C	5.24366300	-1.58679500	-0.34742400
C	6.82146600	0.86486500	0.23591000
C	4.73020600	2.24191600	-0.03291800
C	6.24439900	-1.76658000	-1.31845300
C	4.83007300	-2.71200300	0.38659600
C	7.40231300	0.03215900	1.20831100
C	7.67190600	1.70445900	-0.50400200
C	3.84079400	2.60001900	-1.06113500
C	5.04669900	3.21473300	0.93106300
C	6.83066000	-3.01223800	-1.52477700
H	6.56019500	-0.91900200	-1.91943200
C	5.42222200	-3.95750500	0.18842200
H	4.05117400	-2.60340800	1.13670000
C	8.77955800	0.01579900	1.41110700
H	6.76325000	-0.60437700	1.81311200
C	9.05135200	1.68222900	-0.30978800
H	7.24802100	2.36533400	-1.25547700
C	3.26591700	3.86712700	-1.10589100
H	3.60330700	1.87567900	-1.83457800
C	4.46476100	4.48007700	0.89386800
H	5.73923700	2.96793700	1.73146900
C	6.43936300	-4.13338100	-0.76850800
H	7.58359600	-3.12071200	-2.30063300
H	5.10701200	-4.79706800	0.80196200
C	9.63559300	0.83346800	0.64917700
H	9.19252000	-0.62147700	2.18825600
H	9.68307500	2.31434600	-0.92779200
C	3.55739800	4.83201300	-0.12305600
H	2.60186500	4.11809300	-1.92850900
H	4.69966800	5.19386100	1.67867200
C	7.07470500	-5.45652900	-0.97889300

C	11.10372200	0.80464500	0.85516100
C	2.93147500	6.17568200	-0.16141600
C	8.44751300	-5.56203800	-1.26705200
C	6.32105400	-6.64686600	-0.89539400
C	11.76967200	-0.39902900	1.14917600
C	11.87461600	1.98309500	0.76091000
C	3.65453100	7.32658500	0.21881000
C	1.59740100	6.34027300	-0.57609700
C	9.04234900	-6.80702400	-1.46669800
H	9.05976600	-4.66596300	-1.31328200
C	6.91368700	-7.88857800	-1.09353600
H	5.25436400	-6.59319400	-0.69649900
C	13.14999700	-0.42317500	1.34351300
H	11.20823700	-1.32734000	1.20408100
C	13.25103700	1.95959400	0.95371700
H	11.38318600	2.93040800	0.55747300
C	3.06917300	8.58697500	0.18607600
H	4.69384300	7.23164400	0.52070900
C	1.01001100	7.60418900	-0.60996000
H	1.00684300	5.47141600	-0.85227100
C	8.28681400	-7.98795800	-1.38390300
H	10.10748800	-6.86344000	-1.68061000
H	6.31779800	-8.79417000	-1.03459300
C	13.91170900	0.75299000	1.24941200
H	13.64335500	-1.36769500	1.56238800
H	13.82734000	2.87716400	0.88608900
C	1.73435400	8.74563100	-0.22958800
H	3.64206100	9.46312300	0.47378200
H	-0.02587100	7.70481500	-0.92658000
C	8.94941100	-9.28519100	-1.60303900
C	15.36787400	0.68794400	1.46256100
C	1.07982900	10.06448500	-0.27635900
H	10.02465200	-9.22260900	-1.81923000
H	15.75677400	-0.31571800	1.68205700
H	0.03589200	10.04899500	-0.61807600
N	1.67193300	11.15425000	0.05366800
H	1.03755900	11.94933100	-0.05274200
N	16.13373600	1.71588100	1.40069800
H	17.10389900	1.44692600	1.58040800
N	8.33010900	-10.40798500	-1.54961100
H	8.97658300	-11.17921200	-1.73194200
N	-14.69566600	1.77491800	-4.07906300
N	-14.75126900	-3.51149700	4.17834000
C	-15.18608400	2.94364100	-3.92456100

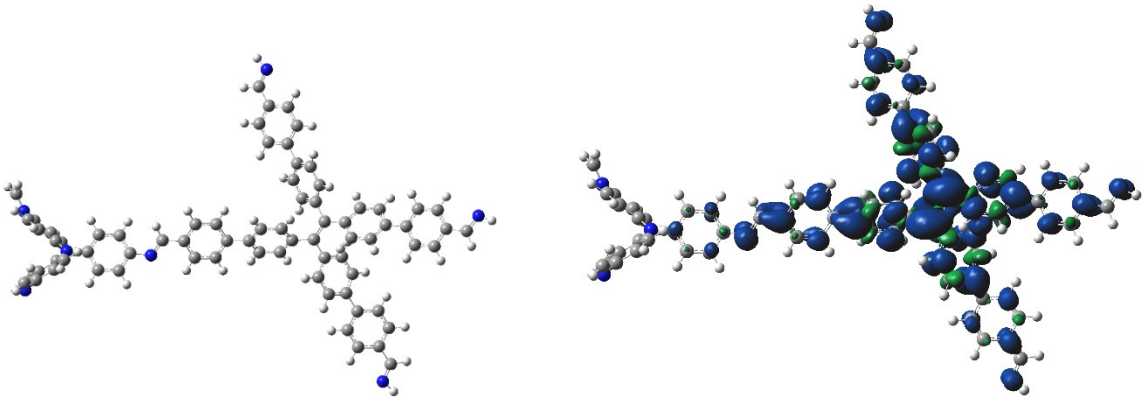
H	-15.08075100	3.53358500	-3.00508700
H	-15.73415600	3.39777200	-4.74977100
C	-14.88603900	-3.00205000	5.34132600
H	-15.42708200	-3.56349200	6.10267000
H	-14.49571500	-2.01626500	5.62496300

Sum of electronic and thermal Free Energies = -3235.524673 (Hartree/Particle).

From TDDFT calculation in acetonitrile, $\boldsymbol{\lambda_{abs}}$ = 491.72 nm.

From TDDFT calculation in absence of any solvent, $\boldsymbol{\lambda_{abs}}$ = 493.27 nm.

Table-S6. DFT-optimized geometry of **[TPA-TPE^{-}]$^{-}$** (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
N	-11.91225000	-1.00677500	0.29498400
C	-12.59377600	-1.64951000	1.35880600
C	-12.08224600	-1.60323500	2.66694000
C	-13.78046300	-2.36684100	1.12265600
C	-12.74534700	-2.24167400	3.71264800
H	-11.15468500	-1.07330200	2.86082400
C	-14.43855700	-3.00761900	2.16793400
H	-14.17828900	-2.42765600	0.11439400
C	-13.94630900	-2.93669600	3.48189500

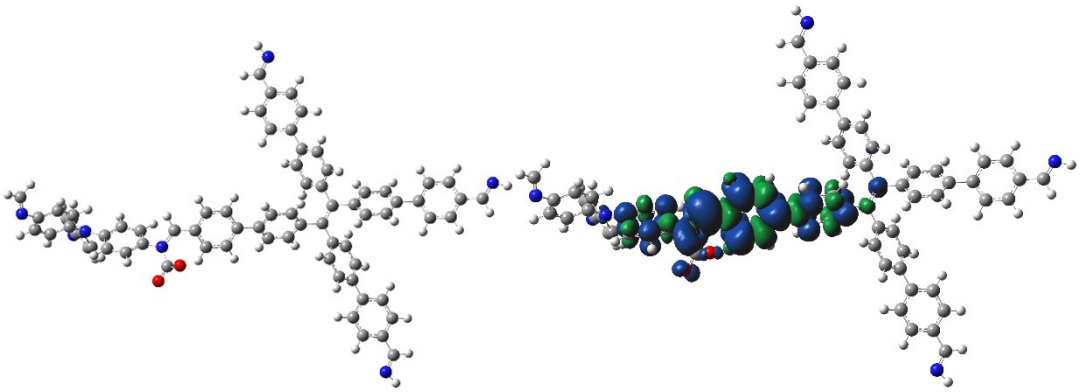
H	-12.31677800	-2.21201400	4.71046300
H	-15.34687800	-3.57219800	1.97539100
C	-12.63822900	-0.33218300	-0.71873700
C	-13.76716600	0.44164000	-0.39957400
C	-12.24826200	-0.43445200	-2.06615100
C	-14.48019000	1.10362900	-1.39651400
H	-14.09182900	0.51518100	0.63386500
C	-12.96480200	0.22405300	-3.06092300
H	-11.38641000	-1.03974800	-2.32951900
C	-14.07683300	1.02090600	-2.74160800
H	-15.36373900	1.67563300	-1.12754500
H	-12.66644900	0.12865800	-4.10146200
C	-10.49219900	-1.05666500	0.23267700
C	-9.75002900	0.09030000	-0.09068000
C	-9.80713500	-2.25935700	0.47553400
C	-8.35963900	0.04144900	-0.16169200
H	-10.26906500	1.02064700	-0.30250900
C	-8.41833000	-2.30644300	0.40815100
H	-10.37032700	-3.15712100	0.71288500
C	-7.66325400	-1.15548400	0.10862600
H	-7.81309300	0.93628300	-0.44552300
H	-7.89503200	-3.24183200	0.58786700
N	-6.26701000	-1.28590700	0.04426800
C	-5.50595500	-0.29792600	0.38069300
C	-4.05412300	-0.32990700	0.27553500
H	-5.92792500	0.63097300	0.79088300
C	-3.35108300	-1.44007600	-0.24328100
C	-3.30188200	0.78307000	0.70431700
C	-1.96689600	-1.43237400	-0.32249200
H	-3.91010100	-2.31195600	-0.57013400
C	-1.91450400	0.79117200	0.61948700
H	-3.81769900	1.65756800	1.09644400
C	-1.20127400	-0.31720700	0.10520400
H	-1.46072300	-2.31691100	-0.69813500
H	-1.37629400	1.68167800	0.93026900
C	0.26606000	-0.31309700	0.01668900
C	0.95833700	-1.08257600	-0.94831000
C	1.06240200	0.46252700	0.89401200
C	2.34359800	-1.06860600	-1.03706300
H	0.39903600	-1.67111900	-1.67099200
C	2.44559000	0.47522500	0.80470400
H	0.58848700	1.03422600	1.68784400
C	3.14580800	-0.28242600	-0.17031500
H	2.82478300	-1.65174800	-1.81758900

H	3.01610400	1.07082800	1.51148100
C	4.60517600	-0.22935000	-0.28030300
C	5.32209700	0.96444800	0.00729900
C	5.31409100	-1.44736900	-0.70125300
C	6.68931000	0.91153300	0.54111300
C	4.72007100	2.28341700	-0.22447400
C	6.47203500	-1.38477000	-1.51499600
C	4.89840700	-2.74161500	-0.30502800
C	7.09695700	-0.11303500	1.43201400
C	7.68133600	1.85882500	0.18586000
C	3.82869200	2.51246500	-1.30317100
C	4.97662800	3.39428300	0.61714600
C	7.17102300	-2.52456800	-1.88791300
H	6.81366100	-0.41452900	-1.86396200
C	5.59499600	-3.88443800	-0.67996300
H	4.02776500	-2.84297700	0.33724700
C	8.39580600	-0.19581700	1.91350200
H	6.36421200	-0.84715600	1.75448700
C	8.98156700	1.77896000	0.66926300
H	7.42752300	2.65336300	-0.51060700
C	3.22963400	3.74606400	-1.51363600
H	3.62049300	1.69795000	-1.99088800
C	4.37943300	4.63103200	0.40612400
H	5.63539400	3.26818100	1.47207200
C	6.75759900	-3.81221300	-1.47841900
H	8.03374100	-2.41868000	-2.54092900
H	5.25306800	-4.84849000	-0.31176300
C	9.38369400	0.74545000	1.54463000
H	8.64079000	-0.98391700	2.62115000
H	9.71008000	2.51028700	0.32822700
C	3.48167000	4.84711100	-0.66315100
H	2.58253200	3.87099400	-2.37827600
H	4.58285100	5.43438900	1.10975400
C	7.50740400	-5.02220100	-1.86537900
C	10.76581000	0.65095600	2.04922000
C	2.83779900	6.15485100	-0.88203500
C	8.90400700	-4.98719600	-2.06524600
C	6.85471700	-6.26469800	-2.05073600
C	11.34984400	-0.59562900	2.36236300
C	11.56146000	1.80684100	2.23992200
C	3.47746100	7.36263800	-0.51048500
C	1.55851100	6.25522300	-1.47109700
C	9.60803800	-6.13083300	-2.43325100
H	9.44860700	-4.06125600	-1.90507400

C	7.55695400	-7.40604400	-2.41430800
H	5.77655500	-6.32559800	-1.93305100
C	12.65372000	-0.68068100	2.84307100
H	10.78653700	-1.51040800	2.20306700
C	12.86297900	1.72195300	2.71566800
H	11.13919100	2.78680100	2.03664600
C	2.87495900	8.59640500	-0.71531500
H	4.47413300	7.32997300	-0.07976700
C	0.95564900	7.49268600	-1.67986400
H	1.01836200	5.35346600	-1.74418200
C	8.95121100	-7.36118800	-2.61360400
H	10.68592400	-6.07309600	-2.57151900
H	7.03143500	-8.34510600	-2.56023400
C	13.43635900	0.47315100	3.02857400
H	13.07729300	-1.65775400	3.06730500
H	13.44895100	2.62435200	2.86268300
C	1.59862800	8.68672100	-1.30643000
H	3.39173400	9.50799300	-0.43039500
H	-0.03483000	7.53503400	-2.12882600
C	9.72900900	-8.54542900	-2.99895000
C	14.80730500	0.34299500	3.53646200
C	0.92985800	9.97181900	-1.54114000
H	10.80672300	-8.36769600	-3.11919900
H	15.12687500	-0.68918800	3.73678300
H	-0.06329100	9.89451700	-2.00518500
N	1.44785800	11.10943300	-1.23584000
H	0.80914500	11.86703100	-1.48818600
N	15.58835400	1.34512700	3.73881200
H	16.49155000	1.02255800	4.09358900
N	9.20890000	-9.70691100	-3.18566000
H	9.93291400	-10.37987500	-3.44743300
N	-14.76243000	1.65547000	-3.80523900
N	-14.66354900	-3.61888600	4.49391700
C	-15.26652800	2.81688200	-3.63924400
H	-15.16548300	3.40044700	-2.71523300
H	-15.82280200	3.27123300	-4.45884200
C	-14.74074200	-3.12343800	5.66829400
H	-15.26542600	-3.68312400	6.44229500
H	-14.31608600	-2.15152200	5.95049700

Sum of electronic and thermal Free Energies = -3235.625227 (Hartree/Particle).

Table-S7. DFT-optimized geometry of **[TPA-TPE^{-}-CO_2]$^{-}$** (doublet) **model-d**, 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
N	-11.28376400	-0.73879700	-0.37440600
C	-12.34269000	-0.42487100	0.51143100
C	-12.10985200	0.35940300	1.65492800
C	-13.64183300	-0.91622100	0.28505900
C	-13.14658100	0.65940800	2.53570300
H	-11.10804100	0.72484000	1.85847700
C	-14.67420800	-0.61920600	1.16920600
H	-13.83520500	-1.54084000	-0.58150700
C	-14.45104400	0.19161300	2.29479000
H	-12.93413700	1.24670000	3.42459600
H	-15.67122800	-1.01485800	0.99489600
C	-11.49619000	-0.78113800	-1.77395900
C	-12.33387700	0.15468800	-2.40585800
C	-10.87357200	-1.76736400	-2.56081200
C	-12.53564200	0.11307900	-3.78354300
H	-12.83579800	0.91234500	-1.81197000
C	-11.08143500	-1.81028200	-3.93611900
H	-10.23287800	-2.50424600	-2.08654800
C	-11.89580100	-0.85933000	-4.57340000
H	-13.20687100	0.83277800	-4.24375200
H	-10.60860300	-2.58442100	-4.53454600
C	-9.98624900	-1.01372700	0.14742700
C	-8.84901000	-0.41528900	-0.41061700

C	-9.82282700	-1.89236100	1.23179800
C	-7.58064500	-0.69767700	0.09467700
H	-8.95668700	0.25962700	-1.25489400
C	-8.56129000	-2.15217100	1.75591900
H	-10.69742200	-2.35935000	1.67569900
C	-7.41334600	-1.56292700	1.19120900
H	-6.70717600	-0.24346400	-0.36398300
H	-8.45820300	-2.82718800	2.59762400
N	-6.12158400	-1.77447800	1.73103000
C	-5.28219200	-0.67272000	1.80251900
C	-3.88549700	-0.66717500	1.57673000
H	-5.78006800	0.27986800	1.97493400
C	-3.15118600	-1.77976400	1.06913400
C	-3.14388500	0.52745100	1.82277400
C	-1.78777000	-1.69660600	0.83962800
H	-3.66809700	-2.70872600	0.85465200
C	-1.77921200	0.59555400	1.59788300
H	-3.66942700	1.40644900	2.19091000
C	-1.05363700	-0.51506100	1.10224000
H	-1.26920600	-2.57689900	0.46862800
H	-1.26445800	1.53525200	1.78065700
C	0.40074000	-0.43955800	0.86224700
C	1.01949700	-1.18834500	-0.16175900
C	1.23442100	0.38066400	1.65294800
C	2.39192400	-1.11588100	-0.38466800
H	0.41593000	-1.81755700	-0.80987700
C	2.60328600	0.46365100	1.41796500
H	0.81009300	0.94002200	2.48209100
C	3.21231900	-0.27165700	0.38501200
H	2.83386600	-1.70349100	-1.18539900
H	3.21677500	1.10077600	2.04857400
C	4.67600600	-0.18958700	0.13186100
C	5.34363300	1.00273600	0.06207800
C	5.37022300	-1.49657500	-0.04054300
C	6.83071000	1.08416700	0.08805700
C	4.63403700	2.30770700	-0.04722400
C	6.24608700	-1.72234700	-1.11678800
C	5.14151700	-2.55637200	0.85400600
C	7.58386200	0.39282800	1.05332000
C	7.52449500	1.88332700	-0.83733000
C	3.60014700	2.50054800	-0.98056100
C	5.00351900	3.39913300	0.75796800
C	6.89248100	-2.94541200	-1.27409600
H	6.41640600	-0.92882900	-1.83840300

C	5.79490700	-3.77771600	0.70448200
H	4.46065900	-2.41221400	1.68870400
C	8.97387700	0.46938900	1.07187800
H	7.06970400	-0.20749600	1.79803100
C	8.91583200	1.95428200	-0.82641800
H	6.96672700	2.43644800	-1.58843900
C	2.94100400	3.72236800	-1.08211100
H	3.31549100	1.68132900	-1.63411700
C	4.33906900	4.62028600	0.66447700
H	5.80601800	3.28134900	1.48137200
C	6.68888900	-3.99702900	-0.36050800
H	7.54398100	-3.09348500	-2.13107300
H	5.62659500	-4.56117300	1.43828300
C	9.67129200	1.24385100	0.12542300
H	9.52281200	-0.05887300	1.84676000
H	9.42150600	2.54836400	-1.58277300
C	3.28909600	4.80669500	-0.25410700
H	2.16289500	3.84328200	-1.83090200
H	4.62315400	5.42981200	1.33130900
C	7.38970800	-5.29415700	-0.51836200
C	11.15241400	1.31133300	0.13465900
C	2.57471900	6.10232900	-0.35027000
C	8.71634500	-5.34811500	-0.98309000
C	6.74707700	-6.51106500	-0.20491900
C	11.92592300	0.17932200	0.44954500
C	11.82820300	2.51135500	-0.17411000
C	3.26132600	7.32555100	-0.19388800
C	1.19067600	6.14833200	-0.59776000
C	9.37365100	-6.56887700	-1.12916300
H	9.24654500	-4.42762800	-1.21008900
C	7.40212900	-7.72850900	-0.34951700
H	5.71482300	-6.50078100	0.13355800
C	13.31852200	0.24460200	0.45703500
H	11.43592800	-0.76535500	0.66741900
C	13.21669600	2.57690900	-0.16773200
H	11.25533600	3.40680000	-0.39846500
C	2.59355100	8.54156100	-0.28127400
H	4.33451700	7.32006100	-0.02496900
C	0.52043200	7.36755200	-0.68620800
H	0.62929700	5.22386300	-0.69844100
C	8.72908800	-7.77645800	-0.81493200
H	10.40231300	-6.58409500	-1.48286600
H	6.88987200	-8.65573600	-0.11200000
C	13.98522900	1.44165900	0.14897800

H	13.89536300	-0.64628100	0.69597800
H	13.72076700	3.51012400	-0.39945800
C	1.20907400	8.58141200	-0.52929200
H	3.13846200	9.47362200	-0.16688600
H	-0.55171900	7.37698600	-0.87012100
C	9.45614200	-9.04677600	-0.98067000
C	15.45772900	1.47210000	0.16632900
C	0.46681100	9.84979700	-0.62780100
H	10.48643600	-8.94349000	-1.34767500
H	15.93511200	0.51707600	0.42483300
H	-0.60966100	9.74027700	-0.81779600
N	1.02226900	11.00008700	-0.50328100
H	0.32710400	11.74300500	-0.60644600
N	16.14168700	2.52547600	-0.09784300
H	17.14228800	2.32586300	-0.02829500
N	8.93821900	-10.19187900	-0.72054400
H	9.61377700	-10.93713500	-0.90512900
N	-12.06606400	-0.96760600	-5.97465300
N	-15.54777300	0.44542000	3.15321700
C	-12.17121100	0.08475900	-6.69037700
H	-12.09115800	1.10463200	-6.29282700
H	-12.33944500	-0.02198600	-7.76179900
C	-15.65463100	1.57425600	3.74083800
H	-16.48657200	1.73396900	4.42641100
H	-14.95935600	2.41006600	3.59054200
C	-5.76652200	-3.08295400	2.34564300
O	-4.91407600	-3.03235100	3.26035200
O	-6.36329200	-4.07687500	1.86762000

Sum of electronic and thermal Free Energies = -3424.227320 (Hartree/Particle).

From TDDFT calculation in acetonitrile, λ_{abs} = 535.77 nm.

Table-S8. 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

N	-12.49490800	-0.93131100	-0.21538300

C	-13.29339800	-1.35090700	0.87896500
C	-12.92585300	-1.03039600	2.19670100
C	-14.45581300	-2.11372000	0.66759500
C	-13.70478000	-1.44865500	3.27339000
H	-12.01941300	-0.46047800	2.37663300
C	-15.23018700	-2.53379500	1.74477300
H	-14.74318900	-2.38358700	-0.34394200
C	-14.88127000	-2.18991000	3.06146100
H	-13.38647500	-1.21010800	4.28428900
H	-16.11904700	-3.13545100	1.57534700
C	-13.10590400	-0.47872800	-1.41303400
C	-14.23953500	0.35002700	-1.37070500
C	-12.59562800	-0.86412000	-2.66531400
C	-14.84043600	0.79223600	-2.54729000
H	-14.65625300	0.63951600	-0.41078500
C	-13.19988700	-0.42498800	-3.83943200
H	-11.72904700	-1.51638400	-2.71254900
C	-14.31617500	0.42707400	-3.80045900
H	-15.73058100	1.41233000	-2.48964700
H	-12.80925900	-0.73818800	-4.80384600
C	-11.07850300	-0.98220200	-0.12018800
C	-10.29067700	0.06957100	-0.61559400
C	-10.43891000	-2.09433800	0.45420300
C	-8.90137700	0.01841400	-0.53001100
H	-10.77132900	0.92456300	-1.08179400
C	-9.05117000	-2.14422300	0.53926300
H	-11.03557400	-2.92136100	0.82719700
C	-8.25630900	-1.08165200	0.07024900
H	-8.31467300	0.83183600	-0.94731000
H	-8.56203200	-3.01162900	0.97431400
N	-6.86004200	-1.20740100	0.18124500
C	-6.13224000	-0.16768600	0.39385000
C	-4.67140600	-0.21131400	0.45804900
H	-6.58208800	0.82194300	0.55778000
C	-3.93978800	-1.39970000	0.26006200
C	-3.95976500	0.97227100	0.72729500
C	-2.55327900	-1.39803400	0.33169700
H	-4.47523400	-2.32307000	0.06088800
C	-2.56943400	0.97269700	0.79675700
H	-4.50308200	1.90353000	0.87302200
C	-1.83043500	-0.21225700	0.60136400
H	-2.01798800	-2.33423200	0.20218000
H	-2.05059300	1.90909400	0.97901800
C	-0.35664900	-0.21634000	0.67378800

C	0.42037400	-1.09527900	-0.11281800
C	0.34391700	0.66745800	1.52623400
C	1.80522100	-1.09302500	-0.05233800
H	-0.06862500	-1.76651200	-0.81374200
C	1.72646200	0.67001300	1.59835900
H	-0.21007200	1.34813900	2.16709900
C	2.52528000	-0.21839600	0.81656800
H	2.35292600	-1.76301300	-0.70603200
H	2.19994800	1.36848300	2.27732400
C	3.95691300	-0.20370200	0.84190500
C	4.73407100	0.83943100	1.67800600
C	4.71834800	-1.21488600	0.07581800
C	6.25681000	0.53503100	1.64384700
C	4.47889500	2.26802300	1.15901000
C	5.62695100	-0.83383500	-0.92970200
C	4.63137700	-2.58368200	0.38933500
C	6.75887500	-0.64002700	2.23222700
C	7.16850500	1.33674700	0.94229300
C	3.93202000	2.49251400	-0.11420700
C	4.87711300	3.40338600	1.88773100
C	6.46199000	-1.76480600	-1.53894600
H	5.69802400	0.21089800	-1.21483700
C	5.46901800	-3.51799900	-0.21726300
H	3.93879100	-2.90561500	1.16163200
C	8.08438800	-1.02811500	2.06551900
H	6.08382100	-1.27920400	2.78921200
C	8.50252800	0.95580300	0.78063800
H	6.83390400	2.24938100	0.46232600
C	3.75526400	3.77963800	-0.62470500
H	3.63881400	1.65088900	-0.73272900
C	4.70388200	4.69082600	1.38277000
H	5.31993300	3.27019700	2.86544200
C	6.42449300	-3.12275900	-1.17179600
H	7.15677200	-1.43220300	-2.30554200
H	5.41758300	-4.55715200	0.09705000
C	8.98269700	-0.25139700	1.31115400
H	8.42450200	-1.95344400	2.52359800
H	9.15837900	1.58285000	0.18197400
C	4.13171200	4.91119600	0.11625600
H	3.34342900	3.89759300	-1.62369800
H	5.00375700	5.53865900	1.99362100
C	7.39345500	-4.09121900	-1.73691900
C	10.36355100	-0.71746900	1.04156400
C	3.94191200	6.28111400	-0.41857000

C	8.72842300	-3.71193500	-1.96932500
C	7.02076900	-5.41993400	-2.03146700
C	10.62359500	-2.07842300	0.79685200
C	11.44788200	0.18406300	0.99052100
C	4.88988200	7.29716400	-0.17002000
C	2.81220100	6.60823800	-1.19044900
C	9.65349600	-4.62367000	-2.47455500
H	9.05419800	-2.70601200	-1.72205700
C	7.94249400	-6.32961400	-2.53727400
H	5.99179700	-5.73384400	-1.87854200
C	11.91392700	-2.52003200	0.50938400
H	9.80545300	-2.79245700	0.79953100
C	12.73563300	-0.25550600	0.70523400
H	11.27733900	1.23747400	1.19531700
C	4.71635000	8.58239700	-0.67030300
H	5.78301700	7.06693300	0.40412700
C	2.63784900	7.89661000	-1.69405300
H	2.05262200	5.85509000	-1.37950100
C	9.27680500	-5.94491400	-2.76668500
H	10.68305700	-4.30901900	-2.63179700
H	7.63724100	-7.34620700	-2.76554000
C	12.98902400	-1.61765300	0.45773200
H	12.08586300	-3.57565900	0.30970900
H	13.56034800	0.45013000	0.67700300
C	3.58461000	8.90311900	-1.44271200
H	5.46000600	9.34914300	-0.47565100
H	1.75175100	8.12660000	-2.28194000
C	10.28367400	-6.87957700	-3.29694700
C	14.33726800	-2.12045100	0.14560200
C	3.36522700	10.25181400	-1.99135300
H	11.28864900	-6.45233500	-3.41711600
H	14.39597500	-3.20406600	-0.02542100
H	2.43872500	10.36763300	-2.57034000
N	4.18321400	11.22544700	-1.81580500
H	3.83693600	12.06779300	-2.28100500
N	15.37210800	-1.36417000	0.07463800
H	16.20097200	-1.91807900	-0.15344100
N	10.02280300	-8.09952000	-3.59933600
H	10.86361400	-8.56607400	-3.94763100
N	-14.88550600	0.82789900	-5.03308700
N	-15.71029100	-2.65881500	4.10880600
C	-15.36412200	2.00444500	-5.16323700
H	-15.32451100	2.77004300	-4.37784700
H	-15.83223900	2.28089200	-6.10772500

C	-15.91144300	-1.93206000	5.13923500
H	-16.52184400	-2.32708400	5.95099800
H	-15.51261600	-0.91645500	5.25772700
C	4.30247200	0.61099900	3.22826700
O	4.34003400	1.59457200	4.00571200
O	4.00829300	-0.57601700	3.52266000

Sum of electronic and thermal Free Energies = -3424.206766 (Hartree/Particle).

Table-S9. DFT-optimized geometry of **model-b** (doublet), computed at the UB3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	-11.44977300	-0.59903300	-0.09899700
C	-12.35783700	-0.75985900	0.97867100
C	-12.06647600	-0.22733900	2.24574900
C	-13.55735900	-1.47272500	0.80391300
C	-12.95510600	-0.39028600	3.30634900
H	-11.13413200	0.30696500	2.40105300
C	-14.44160500	-1.63790500	1.86562000
H	-13.78774000	-1.90444600	-0.16520600
C	-14.16693700	-1.08126700	3.12593700
H	-12.69655300	0.00907200	4.28302300
H	-15.35975700	-2.20247500	1.72759300
C	-11.93508600	-0.32744000	-1.40440600
C	-12.99244800	0.57610800	-1.60166000
C	-11.37607700	-0.97024400	-2.52301800
C	-13.47070800	0.84085400	-2.88317800
H	-13.44684500	1.06457200	-0.74500300
C	-11.85809600	-0.70801400	-3.80191300
H	-10.56854600	-1.68231300	-2.38320200
C	-12.89558000	0.21720000	-4.00512000
H	-14.30531700	1.52477700	-3.00908800
H	-11.43178300	-1.21903300	-4.66092400
C	-10.05311900	-0.72559800	0.12420900
C	-9.14838100	0.15737600	-0.48780800
C	-9.54892300	-1.74871600	0.94595800
C	-7.77754200	0.02988300	-0.27661300

H	-9.52275900	0.93854000	-1.14271400
C	-8.17947700	-1.87478000	1.15612300
H	-10.23606300	-2.44800500	1.41270100
C	-7.26921800	-0.97681800	0.56845000
H	-7.09787100	0.70740700	-0.78561600
H	-7.79513900	-2.67486800	1.78303500
N	-5.89871200	-1.17339400	0.81728500
C	-5.10503700	-0.16456300	0.89534800
C	-3.65871700	-0.29472800	1.08514900
H	-5.48178700	0.86662600	0.83738100
C	-3.01654800	-1.54638900	1.16419900
C	-2.87410700	0.86775400	1.18884400
C	-1.64014300	-1.62573800	1.33859200
H	-3.61202800	-2.45138400	1.09238400
C	-1.49477600	0.78538100	1.36377100
H	-3.34698000	1.84491600	1.11674100
C	-0.84763900	-0.46222600	1.44011700
H	-1.16883200	-2.60186600	1.41390200
H	-0.90993600	1.69921500	1.40785500
C	0.62494500	-0.53838000	1.58420700
C	1.37658400	-1.51004700	0.90535600
C	1.33165200	0.39560500	2.36387100
C	2.77240100	-1.50540300	0.94965900
H	0.87431700	-2.24587000	0.28246600
C	2.72197300	0.39094500	2.41251500
H	0.78713200	1.14274000	2.93568800
C	3.48045800	-0.53669500	1.67566700
H	3.30656900	-2.24067600	0.35861400
H	3.23577100	1.14749100	2.99388400
C	5.02400600	-0.39114900	1.58052700
C	5.39689700	0.88398700	0.78925600
C	5.62110600	-1.65008900	0.92250800
C	6.75856100	1.31105700	0.66525800
C	4.31460900	1.69106900	0.18424300
C	6.09649100	-1.62624300	-0.39797100
C	5.61727800	-2.89713600	1.57338600
C	7.84354100	0.63887400	1.30488600
C	7.11938500	2.41387800	-0.16631800
C	3.45394200	1.14635900	-0.78725200
C	4.05054000	2.99990700	0.62751900
C	6.57942900	-2.77407100	-1.02879400
H	6.08862800	-0.69752800	-0.95862200
C	6.09761400	-4.04647700	0.94840500
H	5.23896900	-2.96011200	2.58474800

C	9.15662900	1.04632500	1.13994900
H	7.65037800	-0.21144800	1.94734200
C	8.43577200	2.82075900	-0.31988600
H	6.34712700	2.94042200	-0.71637900
C	2.33889100	1.84594600	-1.23738500
H	3.64771600	0.15001500	-1.17136700
C	2.93276900	3.70198600	0.18017700
H	4.70112300	3.44382000	1.37542100
C	6.59793300	-4.01181000	-0.36639400
H	6.91957500	-2.70474400	-2.05883500
H	6.09844000	-4.98271300	1.50095900
C	9.49719100	2.15217900	0.32850600
H	9.93714200	0.51265700	1.67570700
H	8.64966300	3.65198300	-0.98655700
C	2.03531100	3.12616900	-0.73833900
H	1.69196100	1.38992100	-1.98207400
H	2.72593200	4.68607300	0.59264400
C	7.11483200	-5.23326900	-1.02945000
C	10.89950100	2.58218200	0.15929300
C	0.78708100	3.82079400	-1.13296400
C	8.22014300	-5.17448000	-1.89775400
C	6.51226700	-6.49095200	-0.81031500
C	11.95737900	1.65117000	0.17974200
C	11.22788400	3.94478000	-0.02834000
C	0.74899400	5.21930200	-1.31708700
C	-0.40741800	3.09807200	-1.30861800
C	8.70234700	-6.32418100	-2.52189000
H	8.72081900	-4.22580600	-2.06887500
C	6.99318400	-7.63812700	-1.43074200
H	5.64299800	-6.56247700	-0.16254000
C	13.27888700	2.06278700	0.02143400
H	11.74343200	0.59269700	0.29480500
C	12.54546800	4.35519800	-0.18676600
H	10.43935600	4.69181600	-0.02215100
C	-0.43184600	5.86685700	-1.66222300
H	1.66136600	5.79886800	-1.20598700
C	-1.59210600	3.74664500	-1.65244700
H	-0.41828700	2.02514900	-1.14222300
C	8.09881900	-7.57260400	-2.29884100
H	9.56343100	-6.25354700	-3.18309500
H	6.51200300	-8.59575900	-1.25674100
C	13.59657900	3.41885400	-0.16461500
H	14.07467000	1.32088700	0.03225900
H	12.77637300	5.40790500	-0.31865200

C	-1.62403400	5.13894100	-1.83487200
H	-0.44237300	6.94267300	-1.80781200
H	-2.50517600	3.16629700	-1.76772100
C	8.63715000	-8.76487800	-2.97480000
C	15.00422100	3.81439900	-0.32709800
C	-2.89511500	5.78929100	-2.19517900
H	9.50379100	-8.57471400	-3.62273100
H	15.72306700	2.98459300	-0.28450900
H	-3.75046000	5.10636000	-2.28995400
N	-3.00985600	7.05343900	-2.38643300
H	-3.97555100	7.28971600	-2.62620800
N	15.37945900	5.02980100	-0.50481200
H	16.39726800	5.07725000	-0.59215700
N	8.14274700	-9.94045100	-2.82826000
H	8.66732600	-10.61816600	-3.38625800
N	-13.34201800	0.42992000	-5.33155100
N	-15.10672700	-1.29617100	4.16256400
C	-13.70014000	1.59709700	-5.70527600
H	-13.64196400	2.48740200	-5.06606400
H	-14.07682100	1.73296200	-6.71880600
C	-15.33020700	-0.37951100	5.02285400
H	-16.02901200	-0.57881100	5.83498000
H	-14.86575800	0.61437900	4.99082800
C	5.51656200	-0.14836000	3.11035900
O	5.48287800	1.05059100	3.48957000
O	5.83948400	-1.14846600	3.79493300

Sum of electronic and thermal Free Energies = -3424.207059 (Hartree/Particle).

Table-S10. 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
N	-11.54908400	-0.79763100	-0.33020000
C	-12.27870300	-2.01113600	-0.47982600
C	-12.07346600	-3.07979900	0.40564200
C	-13.21057100	-2.15241800	-1.52101500
C	-12.79037000	-4.26543400	0.25890700

H	-11.34559800	-2.98111800	1.20531300
C	-13.92158200	-3.33922000	-1.67021600
H	-13.36605100	-1.33294800	-2.21607300
C	-13.73827400	-4.40330100	-0.77112000
H	-12.60260200	-5.09135500	0.93892000
H	-14.63062700	-3.45317000	-2.48541900
C	-12.24819700	0.43806100	-0.43458400
C	-13.48124000	0.61070600	0.21190700
C	-11.72857100	1.48723600	-1.21083000
C	-14.17416800	1.81441600	0.10046800
H	-13.89958200	-0.20365700	0.79569100
C	-12.42445600	2.68649000	-1.32647000
H	-10.78507000	1.35246800	-1.73077700
C	-13.64376800	2.87607500	-0.65441700
H	-15.13815200	1.92387400	0.58899600
H	-12.02855400	3.49128400	-1.93949500
C	-10.16516400	-0.81706300	-0.10195200
C	-9.54770500	0.18645400	0.68422100
C	-9.35078900	-1.84083800	-0.64940200
C	-8.18535400	0.18467100	0.90757700
H	-10.16263500	0.96256700	1.12969700
C	-7.99183000	-1.85208200	-0.42288300
H	-9.80478500	-2.61464300	-1.26034500
C	-7.33604200	-0.83940200	0.35784700
H	-7.76201200	0.95933500	1.53779300
H	-7.37239400	-2.63267900	-0.85641500
N	-6.00741600	-0.93990300	0.50363200
C	-5.31644300	0.09177400	1.24125700
C	-3.81562300	0.01508300	1.01839400
H	-5.65285400	1.09448600	0.94296900
C	-3.16226900	-1.20430200	0.78867200
C	-3.03446600	1.17835200	1.08886500
C	-1.77603500	-1.25781600	0.63290600
H	-3.75034000	-2.11475300	0.73179000
C	-1.64795900	1.12713900	0.94247000
H	-3.51976700	2.13698200	1.25603200
C	-0.98926500	-0.09424500	0.70954900
H	-1.29583400	-2.22009100	0.47199900
H	-1.07316800	2.04929500	0.98004900
C	0.48380800	-0.14712600	0.54144500
C	1.07896900	-0.98347100	-0.42119000
C	1.33538800	0.63672500	1.34294700
C	2.46264700	-1.02277300	-0.58441100
H	0.45024100	-1.59230800	-1.06565200

C	2.71709200	0.60168400	1.17439800
H	0.91111200	1.26373100	2.12280100
C	3.30957600	-0.21456900	0.19433000
H	2.89305000	-1.67238200	-1.34210800
H	3.35001500	1.21213500	1.81166400
C	4.78583700	-0.25157800	0.00283000
C	5.55025800	0.88140900	-0.05231300
C	5.38094500	-1.61116300	-0.13088800
C	7.03704800	0.84101700	0.03329700
C	4.95688100	2.23996500	-0.19783000
C	6.26619200	-1.91775100	-1.17890200
C	5.04587200	-2.63787000	0.76851500
C	7.69055800	0.10325700	1.03595200
C	7.83106300	1.57051900	-0.86857700
C	3.98216600	2.51131600	-1.17396300
C	5.37968500	3.30085700	0.62161100
C	6.81849900	-3.18944500	-1.30517200
H	6.51761900	-1.14900300	-1.90363800
C	5.60559000	-3.90831100	0.65044300
H	4.35556800	-2.43044400	1.58191300
C	9.08013400	0.06915500	1.11412600
H	7.09893900	-0.44469400	1.76327300
C	9.22197300	1.53052500	-0.79794000
H	7.35186500	2.15751700	-1.64768700
C	3.42719800	3.78159400	-1.30236600
H	3.65920300	1.71471900	-1.83772000
C	4.81885000	4.57053800	0.50125900
H	6.13922600	3.12134800	1.37795900
C	6.50799200	-4.21026900	-0.38691600
H	7.47902900	-3.39893400	-2.14210600
H	5.35647800	-4.66700600	1.38728600
C	9.87688100	0.77439100	0.19240900
H	9.55152900	-0.49146300	1.91674900
H	9.80523200	2.07355000	-1.53662500
C	3.82523400	4.83669100	-0.45938800
H	2.69220900	3.96186900	-2.08215000
H	5.13821300	5.35675700	1.17987300
C	7.10797900	-5.56027000	-0.51447800
C	11.35692700	0.72601600	0.26759500
C	3.21796000	6.18394300	-0.58033800
C	8.43759600	-5.72299500	-0.94412600
C	6.36306100	-6.71969100	-0.20979900
C	12.02474500	-0.45862000	0.62744600
C	12.13745000	1.86620300	-0.01994200

C	3.99128900	7.35003200	-0.39544500
C	1.85163700	6.33699300	-0.87781400
C	8.99882300	-6.99318300	-1.06731100
H	9.04500800	-4.84931800	-1.16251900
C	6.92237500	-7.98648800	-0.33139700
H	5.32685100	-6.62473900	0.10249900
C	13.41643900	-0.50121500	0.69855500
H	11.45343600	-1.35980800	0.83111800
C	13.52513500	1.82425300	0.04998200
H	11.64671800	2.80056600	-0.27765500
C	3.42310000	8.61411900	-0.50258600
H	5.05397800	7.26125300	-0.18769400
C	1.28121800	7.60454700	-0.98583100
H	1.22464900	5.45864400	-1.00149200
C	8.25194100	-8.14329500	-0.76432000
H	10.03145700	-7.09283700	-1.39477500
H	6.33246800	-8.86839000	-0.10132200
C	14.18776000	0.63682800	0.41156500
H	13.91037200	-1.43131100	0.97147100
H	14.10990100	2.71319300	-0.16567800
C	2.05570800	8.76121700	-0.79966400
H	4.03363900	9.50126200	-0.36538600
H	0.22017400	7.69712900	-1.20750900
C	8.87813800	-9.46868100	-0.90904600
C	15.65584000	0.55330400	0.49782200
C	1.41777100	10.08347300	-0.91892400
H	9.92262800	-9.44992600	-1.24888700
H	16.04463100	-0.43190800	0.78925900
H	0.34396600	10.05760700	-1.14916400
N	2.05495600	11.18729300	-0.76775500
H	1.42309300	11.98176100	-0.89246800
N	16.43174600	1.54632300	0.25490200
H	17.40927400	1.27052600	0.37441400
N	8.26251800	-10.56738700	-0.66208300
H	8.88011000	-11.36555800	-0.82770600
N	-14.30712700	4.11475300	-0.82186100
N	-14.48409100	-5.58680500	-0.98466600
C	-14.90634000	4.65291600	0.16843800
H	-14.90435100	4.23358900	1.18266300
H	-15.44500100	5.58745900	0.01362800
C	-14.94951300	-6.23331100	0.01270100
H	-15.48798700	-7.16340800	-0.16747300
H	-14.84949100	-5.90180400	1.05412800
C	-5.56738600	0.02287400	2.82077400

O	-5.51515000	1.13478900	3.41095900
O	-5.76455100	-1.11026900	3.32542200

Sum of electronic and thermal Free Energies = -3424.218842 (Hartree/Particle).

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

Atom	x	y	z
N	11.71334000	-0.63381900	0.08741300
C	12.54517400	-0.95854200	-1.00673000
C	12.10657900	-0.73572300	-2.32572000
C	13.80674900	-1.55507300	-0.81329500
C	12.91110300	-1.07093600	-3.41195400
H	11.12329800	-0.30872200	-2.49610900
C	14.60395100	-1.89556700	-1.90127100
H	14.15380500	-1.76237500	0.19403500
C	14.18411000	-1.63746700	-3.21718700
H	12.53517300	-0.90825000	-4.41823600
H	15.56923000	-2.36856600	-1.74084100
C	12.24373200	-0.17068100	1.31264100
C	13.35811000	0.68885500	1.34701600
C	11.65553300	-0.55364700	2.53320400
C	13.86358600	1.15323000	2.55852600
H	13.83432600	0.98753300	0.41833200
C	12.16862900	-0.09420200	3.74236100
H	10.79883300	-1.22008000	2.52642700
C	13.26519800	0.78323100	3.77727900
H	14.73942100	1.79613000	2.55455300
H	11.71707800	-0.40906400	4.67948000
C	10.29738800	-0.79660000	-0.03935400
C	9.42603400	0.26473100	0.23899300
C	9.74918400	-2.02832900	-0.43231300
C	8.04721800	0.10672100	0.12689500
H	9.83585200	1.21703300	0.56737700
C	8.37516900	-2.18776400	-0.56559200
H	10.41362600	-2.86230500	-0.64436100
C	7.47201000	-1.12336400	-0.30128200

H	7.40003300	0.93662500	0.39379100
H	7.98510300	-3.15252300	-0.87292900
N	6.10893100	-1.31799800	-0.43137600
C	5.30420700	-0.27167700	-0.67556700
C	3.88925300	-0.29730200	-0.54747100
H	5.74301800	0.66409600	-1.04027700
C	3.16778400	-1.37282000	0.05808700
C	3.10384900	0.79688500	-1.02414800
C	1.78628800	-1.35592500	0.14976000
H	3.71635300	-2.21483300	0.46823900
C	1.72456300	0.80252200	-0.93031600
H	3.61062400	1.65117400	-1.47077100
C	1.00734400	-0.27744800	-0.34427800
H	1.29044000	-2.21197700	0.60068500
H	1.18362500	1.67401600	-1.29002400
C	-0.45822900	-0.26830900	-0.24780000
C	-1.14809400	-1.00553800	0.74484400
C	-1.25778200	0.47631700	-1.14956200
C	-2.53603800	-0.99135200	0.83323100
H	-0.58795200	-1.57824300	1.47841600
C	-2.64313600	0.50232100	-1.04754600
H	-0.78769100	1.01950900	-1.96437900
C	-3.32148100	-0.21862100	-0.04484900
H	-3.02343700	-1.56667500	1.61658800
H	-3.21872400	1.08113800	-1.76443000
C	-4.79984100	-0.18948200	0.06998400
C	-5.52761200	0.96907000	-0.03094600
C	-5.45617900	-1.50673300	0.30464700
C	-7.00351400	0.96417900	-0.22405600
C	-4.89709500	2.31509500	0.04888900
C	-6.42116300	-1.67140200	1.31388300
C	-5.10595400	-2.63427100	-0.45818800
C	-7.61170500	0.14600000	-1.19332800
C	-7.83576600	1.80292700	0.53889800
C	-3.97068700	2.62877000	1.06015300
C	-5.23766300	3.32963200	-0.86335900
C	-7.03423000	-2.90245100	1.53045800
H	-6.68791000	-0.82231300	1.93630900
C	-5.72468900	-3.86515300	-0.25007100
H	-4.35566900	-2.53697100	-1.23831400
C	-8.99258600	0.14071500	-1.36913200
H	-6.98965900	-0.48861500	-1.81758000
C	-9.21851000	1.79372900	0.37034000
H	-7.39350200	2.45260500	1.28957900

C	-3.38693000	3.88962800	1.13706700
H	-3.71061000	1.87151700	1.79382800
C	-4.64823500	4.59025800	-0.79357000
H	-5.95670600	3.11938600	-1.65076400
C	-6.70654900	-4.02461700	0.74597500
H	-7.75767100	-2.99964400	2.33544600
H	-5.45927200	-4.70544000	-0.88590000
C	-9.82861900	0.95771700	-0.58421700
H	-9.42452100	-0.48636200	-2.14438400
H	-9.83300400	2.42475600	1.00672400
C	-3.70506700	4.89684800	0.20520800
H	-2.69431900	4.10310700	1.94670400
H	-4.90495800	5.33603200	-1.54105300
C	-7.37056900	-5.33178200	0.96685200
C	-11.30021000	0.94092500	-0.76171900
C	-3.06920100	6.23387400	0.27640000
C	-8.73271100	-5.40243600	1.31124800
C	-6.65582800	-6.54194900	0.83753400
C	-11.97981400	-0.25379500	-1.06242000
C	-12.06268100	2.12197700	-0.63324200
C	-3.79317300	7.40292100	-0.04328300
C	-1.72359400	6.37595900	0.66234100
C	-9.35444100	-6.63263500	1.52030600
H	-9.31630000	-4.49001100	1.39425200
C	-7.27533700	-7.76893900	1.04482100
H	-5.59714300	-6.51581000	0.59512400
C	-13.36366200	-0.26679200	-1.23023500
H	-11.42558800	-1.18452600	-1.14320900
C	-13.44270100	2.10953300	-0.79906100
H	-11.56192100	3.06320700	-0.42445200
C	-3.19828800	8.65758100	0.01905000
H	-4.84059100	7.32559900	-0.32119000
C	-1.12666300	7.63413300	0.72620800
H	-1.13176100	5.49435000	0.89120600
C	-8.63761300	-7.83341500	1.39103600
H	-10.41096100	-6.66170800	1.77805000
H	-6.70849100	-8.69001400	0.95009300
C	-14.11661900	0.91186100	-1.10161800
H	-13.86678600	-1.20479800	-1.45495800
H	-14.01196100	3.02922500	-0.70507400
C	-1.85206700	8.79326600	0.40551100
H	-3.77212800	9.54698200	-0.22249400
H	-0.08219700	7.71679800	1.01907600
C	-9.32802300	-9.11402100	1.62091300

C	-15.57673700	0.85858100	-1.28671700
C	-1.18702400	10.10495500	0.48177200
H	-10.39042300	-9.02357400	1.88556400
H	-15.97578200	-0.13901800	-1.51566300
H	-0.13422200	10.07012600	0.79360300
N	-1.77922500	11.21041200	0.20788000
H	-1.13552700	11.99638600	0.32538500
N	-16.33574200	1.88932200	-1.19192100
H	-17.31065900	1.62827000	-1.35690300
N	-8.74557200	-10.25357200	1.52378100
H	-9.40615700	-11.00822400	1.72381400
N	13.73270800	1.20449600	5.04529200
N	15.05027700	-2.01544500	-4.27094400
C	14.21902800	2.37599900	5.19639300
H	14.26308900	3.12815500	4.39837400
H	14.60660400	2.66258000	6.17380900
C	15.09559500	-1.32748900	-5.34643100
H	15.74317300	-1.66083700	-6.15711200
H	14.52552200	-0.40347200	-5.50682700
C	5.43617800	-3.25821000	-1.18831000
O	5.10361300	-2.97634800	-2.29462900
O	5.61233000	-3.99441200	-0.26949800

Sum of electronic and thermal Free Energies = -3424.209184 (Hartree/Particle).

Table-S12. DFT-optimized geometry of **[TPA-TPE^{-}-CO$_2^{-}$]$^{2-}$** (singlet), computed at the B3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	-10.26024000	-0.51541700	-0.75681400
C	-11.49317600	-0.32156500	-0.09570200
C	-11.53358700	-0.14909400	1.30068800
C	-12.71135100	-0.34159600	-0.80279400
C	-12.74581700	0.02479500	1.96384100
H	-10.60794900	-0.16500700	1.86740500
C	-13.92077100	-0.17544100	-0.13565600
H	-12.70611600	-0.50114000	-1.87642500
C	-13.95978700	0.03656100	1.25277600

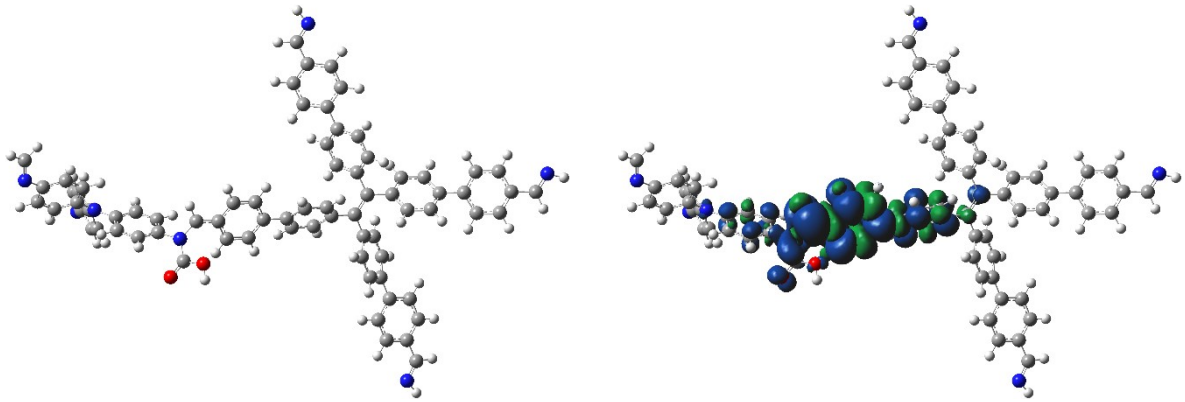
H	-12.74636500	0.13194800	3.04499400
H	-14.85570100	-0.20766000	-0.68892800
C	-10.02652100	-0.01037600	-2.05570400
C	-10.54696700	1.23362600	-2.45941400
C	-9.25299600	-0.74317100	-2.97604700
C	-10.29828300	1.73040700	-3.73633000
H	-11.15568600	1.81008500	-1.76979100
C	-9.01347500	-0.24735100	-4.25405900
H	-8.84808900	-1.70710100	-2.68469200
C	-9.51112600	1.00523900	-4.64986000
H	-10.73284900	2.68265100	-4.02753700
H	-8.42821300	-0.82859100	-4.96174500
C	-9.22403400	-1.25579100	-0.10287900
C	-7.94498700	-0.70630400	0.05522400
C	-9.46915300	-2.54297000	0.39526000
C	-6.93489300	-1.43083500	0.68510400
H	-7.73984600	0.28927100	-0.33028500
C	-8.46664400	-3.26174700	1.04209400
H	-10.46169900	-2.97397000	0.28968400
C	-7.16821900	-2.72704900	1.19212200
H	-5.94841400	-0.99366300	0.80172900
H	-8.67730400	-4.25427400	1.42192700
N	-6.14400600	-3.40686000	1.88420400
C	-5.28517500	-2.61179800	2.70130400
C	-3.97098400	-2.33837500	2.38599300
H	-5.74541200	-2.16569300	3.58450700
C	-3.31169700	-2.81958800	1.18804800
C	-3.13146500	-1.52516300	3.24453700
C	-2.00045300	-2.51352900	0.89986500
H	-3.88450400	-3.42838800	0.49232800
C	-1.82811000	-1.22269000	2.92978700
H	-3.55707900	-1.14596100	4.17357700
C	-1.18088900	-1.69807700	1.74234400
H	-1.59174200	-2.89480800	-0.03331200
H	-1.26924000	-0.61466400	3.63732200
C	0.19230200	-1.36842200	1.41559800
C	0.92161600	-2.03713500	0.38594900
C	0.92304100	-0.35252900	2.10507000
C	2.23261800	-1.71136900	0.07237800
H	0.45392900	-2.84637500	-0.16681000
C	2.22705700	-0.02202800	1.77616900
H	0.44942800	0.19997500	2.91096100
C	2.93083100	-0.67624900	0.73788300
H	2.73339200	-2.26261100	-0.72061800

H	2.72495300	0.76643100	2.33440100
C	4.30724200	-0.31063900	0.37110400
C	4.76720800	0.99251000	0.35409500
C	5.20925300	-1.43883100	-0.00073900
C	6.21718000	1.31388600	0.35002200
C	3.84641500	2.15812700	0.32717900
C	5.99475500	-1.38911700	-1.16600600
C	5.28524000	-2.59901500	0.78935400
C	7.12097600	0.65175700	1.20445400
C	6.74233300	2.30954600	-0.49715100
C	2.72531500	2.18628100	-0.52608500
C	4.08231000	3.29681500	1.12094400
C	6.84271700	-2.43823900	-1.51091000
H	5.93374000	-0.51457900	-1.80736500
C	6.13884400	-3.64729400	0.45233900
H	4.68278500	-2.66595200	1.69125900
C	8.48188100	0.94157400	1.18670900
H	6.74385300	-0.09687700	1.89482900
C	8.10391900	2.59969900	-0.51912300
H	6.07352500	2.84460300	-1.16618600
C	1.87020300	3.28197400	-0.56316200
H	2.52922500	1.33215700	-1.16749300
C	3.22446100	4.39449800	1.08939500
H	4.94004000	3.31120000	1.78832300
C	6.94104100	-3.58720300	-0.70302000
H	7.41653900	-2.37584000	-2.43174500
H	6.20277900	-4.51074500	1.10913500
C	9.00867000	1.91716600	0.31777300
H	9.14046300	0.42430900	1.87947500
H	8.47300100	3.34542800	-1.21826600
C	2.09404300	4.41140700	0.25084900
H	1.03182900	3.27391200	-1.25471100
H	3.42072600	5.23638900	1.74814300
C	7.85713000	-4.69711600	-1.05915900
C	10.45909300	2.21572600	0.28944000
C	1.17285600	5.57054200	0.22291800
C	9.11433900	-4.44148400	-1.63665200
C	7.49603700	-6.04187400	-0.82727700
C	11.41313200	1.19885000	0.48343000
C	10.93035700	3.52832600	0.06582300
C	1.65340900	6.88963700	0.37895000
C	-0.21180700	5.39267500	0.04098600
C	9.97485100	-5.48680700	-1.96885500
H	9.43167600	-3.41648200	-1.80595600

C	8.35395800	-7.08465000	-1.15713100
H	6.52130300	-6.26966700	-0.40502700
C	12.77758100	1.48206100	0.45778500
H	11.08633100	0.17368400	0.63229600
C	12.29078900	3.81109900	0.03762100
H	10.21819200	4.33856400	-0.06286800
C	0.79085200	7.97901400	0.35465700
H	2.71980500	7.06071000	0.49654400
C	-1.07721800	6.48487900	0.01478900
H	-0.61882000	4.39034600	-0.05608100
C	9.61035500	-6.82279000	-1.73413300
H	10.94528100	-5.26296500	-2.40679800
H	8.05581000	-8.11337900	-0.97979600
C	13.23913900	2.78984100	0.23399700
H	13.49414900	0.67637500	0.60312600
H	12.63379400	4.82809000	-0.12700800
C	-0.59241100	7.79406000	0.17132300
H	1.18034400	8.98622600	0.46730000
H	-2.14410400	6.31903100	-0.11886100
C	10.54747900	-7.89970200	-2.09597800
C	14.68774200	3.04964200	0.21197200
C	-1.53776500	8.92160300	0.13940300
H	11.49220700	-7.55742500	-2.54014800
H	15.31673300	2.16449000	0.37860000
H	-2.58871300	8.63678900	-0.00739100
N	-1.17804200	10.14729600	0.27116900
H	-1.99249600	10.76348100	0.21774600
N	15.19164000	4.21408500	0.01514700
H	16.21289400	4.16731000	0.04077400
N	10.29408700	-9.14459600	-1.91257600
H	11.07815900	-9.71719800	-2.23391300
N	-9.22895900	1.44140700	-5.96680500
N	-15.22889500	0.19594100	1.85911300
C	-9.04975800	2.68253400	-6.20969200
H	-9.05294800	3.46377400	-5.43885500
H	-8.87089800	2.99691000	-7.23773800
C	-15.36798500	0.96358500	2.87068300
H	-16.34764600	1.04031000	3.34193100
H	-14.55715500	1.56833100	3.29653500
C	-5.98467200	-4.84245000	1.79827500
O	-5.25089000	-5.38096300	2.67324400
O	-6.57627700	-5.42775000	0.84409800

Sum of electronic and thermal Free Energies = -3424.329812 (Hartree/Particle).

Table-S13. DFT-optimized geometry of **[TPA-TPE-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
N	10.82356600	-0.81991500	0.58360400
C	11.99454700	-0.26082900	0.00569800
C	11.90839000	0.83341500	-0.86997500
C	13.25892800	-0.80422500	0.29091500
C	13.05742300	1.37867200	-1.43919000
H	10.93567300	1.25041700	-1.11289000
C	14.40541100	-0.26072100	-0.28092000
H	13.33676600	-1.65934400	0.95535300
C	14.32546400	0.85116300	-1.13590500
H	12.96554400	2.20865700	-2.13398700
H	15.37910900	-0.69370200	-0.06858100
C	10.82561300	-1.19573500	1.95343000
C	11.42820000	-0.37227600	2.91790500
C	10.24501200	-2.40845200	2.36327300
C	11.43886600	-0.74331500	4.26103200
H	11.89898000	0.55675500	2.61087600
C	10.25955700	-2.77935100	3.70449100
H	9.79107100	-3.06191900	1.62456600
C	10.83546200	-1.94392100	4.67614600
H	11.93228300	-0.10326200	4.98693100

H	9.82193400	-3.72447400	4.01412000
C	9.66162200	-1.01065700	-0.20310400
C	8.38592000	-0.76760600	0.33398800
C	9.76345300	-1.44645500	-1.53720100
C	7.24455300	-0.96952800	-0.43820000
H	8.28939700	-0.42805900	1.36024100
C	8.62386200	-1.62213600	-2.31592400
H	10.74207000	-1.63732000	-1.96590300
C	7.35593700	-1.39620100	-1.76641700
H	6.26188200	-0.78375500	-0.01453500
H	8.71691100	-1.95420700	-3.34454000
N	6.16260400	-1.53322900	-2.55418900
C	5.30329500	-0.41116000	-2.58946500
C	3.92873000	-0.43790600	-2.27025900
H	5.80463900	0.53374800	-2.77773100
C	3.25089000	-1.59259200	-1.78212800
C	3.15958700	0.75545600	-2.40969200
C	1.90319200	-1.54930500	-1.46662500
H	3.79806500	-2.51991000	-1.64632200
C	1.81174500	0.78310400	-2.09698900
H	3.64868900	1.66050000	-2.76232700
C	1.14034000	-0.36772500	-1.61930600
H	1.42087300	-2.45622000	-1.11283200
H	1.26910700	1.71906500	-2.19584400
C	-0.29808400	-0.32999200	-1.28409700
C	-0.83151300	-1.12202600	-0.24653400
C	-1.19160100	0.49935500	-1.99317900
C	-2.18649900	-1.07787600	0.07139500
H	-0.17521700	-1.76034700	0.33824400
C	-2.54271000	0.55143700	-1.66479500
H	-0.83101700	1.09161300	-2.82951600
C	-3.06710200	-0.22318700	-0.61486500
H	-2.56544000	-1.69560100	0.88146800
H	-3.20732600	1.19701700	-2.23143600
C	-4.51161500	-0.16783200	-0.25922200
C	-5.17607100	1.01558000	-0.08940900
C	-5.18305700	-1.48800600	-0.10174800
C	-6.66119700	1.09205900	-0.00684700
C	-4.46202300	2.31771700	0.02802200
C	-5.98947200	-1.76945200	1.01499200
C	-5.00102800	-2.50548200	-1.05437500
C	-7.48030600	0.43485100	-0.94172600
C	-7.28763400	1.85589900	0.99330900
C	-3.37080700	2.47522100	0.90046200

C	-4.88364700	3.43960200	-0.70642700
C	-6.61538900	-3.00486100	1.15712400
H	-6.12160000	-1.01001600	1.77992900
C	-5.63403600	-3.73917700	-0.91898600
H	-4.37443100	-2.31808200	-1.92233900
C	-8.86810500	0.51144900	-0.86159700
H	-7.02012500	-0.13768000	-1.74157800
C	-8.67623500	1.92653800	1.08077300
H	-6.67845500	2.38210400	1.72347100
C	-2.70849500	3.69471900	1.01108600
H	-3.04428100	1.63098000	1.50044900
C	-4.21625300	4.65836700	-0.60459400
H	-5.73067200	3.34841000	-1.38125700
C	-6.45952100	-4.01365400	0.18754000
H	-7.21235100	-3.19698400	2.04452200
H	-5.50472200	-4.48853500	-1.69510900
C	-9.49686100	1.25165000	0.15760300
H	-9.47022000	0.01132600	-1.61533800
H	-9.12752900	2.49286700	1.89083200
C	-3.11087600	4.81095000	0.25336100
H	-1.88486800	3.78783600	1.71373000
H	-4.54335000	5.49396200	-1.21731300
C	-7.13955300	-5.32349400	0.33037200
C	-10.97491800	1.32206000	0.25169900
C	-2.39643300	6.10575200	0.36107400
C	-8.43763200	-5.41005700	0.86531200
C	-6.50529400	-6.51955000	-0.06833200
C	-11.77323200	0.20343600	-0.04833300
C	-11.62227300	2.51241000	0.64655800
C	-3.09679500	7.32977400	0.30415100
C	-0.99974700	6.15014000	0.52235500
C	-9.07569100	-6.64264200	0.99697100
H	-8.96170200	-4.50505700	1.15907400
C	-7.14106700	-7.74876500	0.06221500
H	-5.49371900	-6.48425900	-0.46299800
C	-13.16283000	0.27211900	0.04187300
H	-11.30363600	-0.73414800	-0.33184400
C	-13.00763100	2.58141900	0.73714500
H	-11.03116200	3.39831700	0.86130900
C	-2.43000000	8.54523500	0.40561100
H	-4.17850300	7.32430500	0.20317300
C	-0.33043700	7.36882800	0.62469000
H	-0.42930100	5.22600400	0.54494600
C	-8.43954000	-7.82951100	0.59812400

H	-10.08300900	-6.68316600	1.40579000
H	-6.63520000	-8.66008400	-0.24139400
C	-13.80128500	1.45939400	0.43575400
H	-13.75853200	-0.60892600	-0.18708400
H	-13.49028900	3.50759600	1.03351300
C	-1.03292400	8.58355400	0.56829800
H	-2.98502500	9.47759700	0.36928400
H	0.75116700	7.37762700	0.74056200
C	-9.14569900	-9.11316800	0.75170600
C	-15.27145800	1.49420600	0.52121400
C	-0.29174800	9.85155300	0.68086200
H	-10.15420200	-9.03576600	1.18031900
H	-15.77067300	0.55165000	0.25832400
H	0.79438700	9.74131600	0.80356000
N	-0.85895300	11.00207500	0.64092600
H	-0.16268300	11.74484400	0.73747300
N	-15.92989600	2.53786700	0.87383600
H	-16.93399800	2.34392800	0.86516100
N	-8.63416500	-10.24111500	0.41532000
H	-9.29205500	-11.00034100	0.60666000
N	10.82411100	-2.38710400	6.02058600
N	15.52975800	1.34708800	-1.69074500
C	10.65258200	-1.54761500	6.96703700
H	10.46137700	-0.47871800	6.80732200
H	10.68489300	-1.90160800	7.99718900
C	15.68764900	2.60358800	-1.85262000
H	16.60581300	2.96345000	-2.31636400
H	14.95236100	3.35639100	-1.54078300
C	5.96624200	-2.68296100	-3.28991500
O	4.94266100	-2.55859000	-4.16663300
O	6.63405000	-3.70460300	-3.18340700
H	4.84254200	-3.41854200	-4.61357900

Sum of electronic and thermal Free Energies = -3424.669977 (Hartree/Particle).

From TDDFT calculation in acetonitrile, λ_{abs} = 519.98 nm.

Table-S14. DFT-optimized geometry of **[TPA-TPE^{-}-COOH]**$^{-}$ (singlet), computed at the B3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	10.09758000	-0.94505200	0.90224000
C	11.34598100	-0.31045200	0.68949200
C	11.43512100	0.83929600	-0.11434700
C	12.52494800	-0.83271400	1.25219200
C	12.66269700	1.45951700	-0.33565500
H	10.53808000	1.23990200	-0.57646500
C	13.75070600	-0.21441800	1.02522900
H	12.47666500	-1.73149100	1.85914100
C	13.83786900	0.95321600	0.24880800
H	12.70762600	2.33240100	-0.98088600
H	14.65888800	-0.63257900	1.45102200
C	9.77096600	-1.49424300	2.16639400
C	10.13190400	-0.83402400	3.35391700
C	9.08278100	-2.71780500	2.25766300
C	9.80640300	-1.37462800	4.59576300
H	10.67832700	0.10268800	3.30180800
C	8.76363800	-3.25852900	3.49961200
H	8.80731600	-3.24598500	1.35017600
C	9.09895300	-2.58716900	4.68706700
H	10.11797400	-0.85678900	5.49858200
H	8.24479300	-4.21133300	3.56179400
C	9.16752700	-1.05243400	-0.17152100
C	7.81216700	-0.74177500	0.02668200
C	9.58897700	-1.46589300	-1.44347800
C	6.90133300	-0.85266400	-1.02069900
H	7.47459700	-0.41968400	1.00746700
C	8.67937600	-1.55986200	-2.49638000
H	10.63597700	-1.70179600	-1.61027900
C	7.32445700	-1.26456900	-2.29262700
H	5.85671600	-0.60257800	-0.86555900
H	9.01826400	-1.88046600	-3.47573200
N	6.37473500	-1.30759800	-3.36658000
C	5.49966700	-0.17885900	-3.53539000
C	4.17685900	-0.20197400	-3.12161200
H	5.96241100	0.70826000	-3.95968900
C	3.54585200	-1.34153700	-2.49608400
C	3.31212300	0.94474100	-3.28906300
C	2.22723600	-1.31687000	-2.08519800
H	4.12851000	-2.24801600	-2.34790300
C	1.99573900	0.94110100	-2.88160500
H	3.72707800	1.84416400	-3.74308100

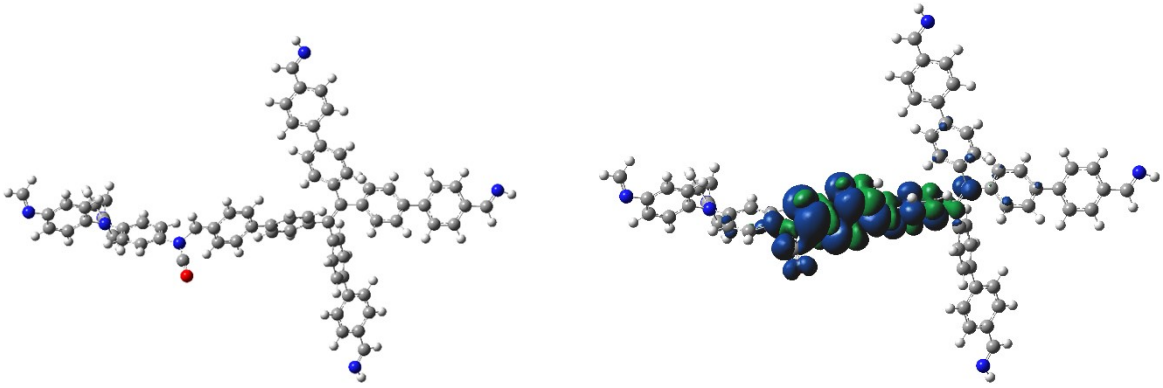
C	1.38192400	-0.18505900	-2.25545000
H	1.82256100	-2.22266800	-1.63828700
H	1.42039300	1.85401600	-3.02078300
C	-0.01003100	-0.17179800	-1.81882300
C	-0.51484900	-1.08942100	-0.85719700
C	-0.95663500	0.75795300	-2.33310100
C	-1.84077000	-1.07043800	-0.44280300
H	0.15333100	-1.81671100	-0.40493600
C	-2.27474300	0.78624000	-1.90057600
H	-0.65817900	1.45297400	-3.11270400
C	-2.75971700	-0.11687900	-0.93057400
H	-2.16937800	-1.79108400	0.30264300
H	-2.95691900	1.51334600	-2.33288000
C	-4.15949300	-0.08345500	-0.45772500
C	-4.84010100	1.08434800	-0.20401000
C	-4.81034100	-1.41078400	-0.26044500
C	-6.31936000	1.11821700	-0.04764300
C	-4.15099100	2.39517200	-0.05927300
C	-5.49714900	-1.71542100	0.92774500
C	-4.73126000	-2.40957600	-1.24611400
C	-7.16881600	0.45522200	-0.95307800
C	-6.92173300	1.83871700	1.00045900
C	-2.99673500	2.53129100	0.73485000
C	-4.65603700	3.55362400	-0.67708400
C	-6.10644800	-2.95396500	1.11128000
H	-5.54853800	-0.96959000	1.71568300
C	-5.34847900	-3.64619700	-1.07010300
H	-4.19816600	-2.20260900	-2.17018800
C	-8.55188000	0.47939800	-0.79765500
H	-6.73414700	-0.08154700	-1.79107900
C	-8.30504900	1.86051400	1.16136000
H	-6.29371100	2.36849400	1.71192000
C	-2.36048100	3.75997100	0.87974200
H	-2.59894600	1.65797900	1.24325400
C	-4.01714300	4.78432500	-0.53899200
H	-5.54989300	3.48309700	-1.29134700
C	-6.05390600	-3.94355600	0.11136000
H	-6.60736600	-3.16412400	2.05251300
H	-5.30303800	-4.37978200	-1.87051200
C	-9.15213900	1.17523100	0.26927500
H	-9.17496600	-0.02556000	-1.53105000
H	-8.73033200	2.39378000	2.00735800
C	-2.85107500	4.91459200	0.23811200
H	-1.48599800	3.83023500	1.52116100

H	-4.41474800	5.64824800	-1.06489100
C	-6.71538200	-5.25708300	0.29967200
C	-10.62381800	1.18907900	0.44321500
C	-2.16350500	6.21968200	0.37860600
C	-7.94795800	-5.35756300	0.97028900
C	-6.12814200	-6.44399800	-0.18883600
C	-11.39979300	0.05467100	0.14127600
C	-11.29078400	2.33924500	0.91820800
C	-2.89530200	7.42517000	0.44854800
C	-0.75985500	6.29586900	0.44384000
C	-8.56724300	-6.59404900	1.14700300
H	-8.43754200	-4.45966800	1.33647200
C	-6.74551400	-7.67710000	-0.01399500
H	-5.16533500	-6.39868800	-0.69010400
C	-12.78408200	0.07007700	0.30493100
H	-10.91502200	-0.85472300	-0.20206800
C	-12.67079500	2.35483200	1.08321200
H	-10.72028400	3.23752700	1.13705400
C	-2.25302300	8.65106400	0.57663300
H	-3.98108400	7.39492100	0.42530700
C	-0.11503700	7.52499800	0.57334800
H	-0.16627400	5.38931800	0.36806300
C	-7.97778500	-7.77167200	0.65869700
H	-9.52419300	-6.64487200	1.66198600
H	-6.27488500	-8.58094500	-0.38841900
C	-13.44144300	1.21766400	0.77793500
H	-13.36053200	-0.82259100	0.07163900
H	-13.16799400	3.25121200	1.44103700
C	-0.84893600	8.72072600	0.64064900
H	-2.83218700	9.56734600	0.63783500
H	0.97168900	7.55781800	0.61234900
C	-8.66234300	-9.05948200	0.86447300
C	-14.90508400	1.19666600	0.93801400
C	-0.13290300	10.00038700	0.77362000
H	-9.61689700	-8.99231100	1.40406500
H	-15.38467300	0.24653100	0.66567300
H	0.96162900	9.91393700	0.81118100
N	-0.72809300	11.13588300	0.84084900
H	-0.04364200	11.89051400	0.92987100
N	-15.58071100	2.20294000	1.36084700
H	-16.57658400	1.97288100	1.39462200
N	-8.19197400	-10.18004900	0.45161800
H	-8.82489700	-10.94375700	0.70056300
N	8.74834000	-3.19969200	5.91432000

N	15.11929000	1.52300100	0.05538100
C	8.38636200	-2.48301000	6.90727400
H	8.27890700	-1.39154100	6.86606900
H	8.15713100	-2.97222500	7.85372900
C	15.25305300	2.79104700	-0.01517100
H	16.24318700	3.20621400	-0.20201800
H	14.42589300	3.50096800	0.11255200
C	6.31706800	-2.42339600	-4.15018500
O	5.45780600	-2.29063000	-5.19856300
O	6.94332600	-3.47109700	-3.96745700
H	5.47960800	-3.14252500	-5.66999200

Sum of electronic and thermal Free Energies = -3424.789558 (Hartree/Particle).

Table-S15. DFT-optimized geometry of **[TPA-TPE-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
N	10.35221400	-1.00782200	0.64201100
C	11.71966800	-0.68880900	0.38356000
C	12.06884500	0.53825700	-0.19691000
C	12.72908300	-1.60336900	0.71942400
C	13.40615300	0.84955400	-0.43639400
H	11.29008400	1.24525100	-0.46770200
C	14.06463400	-1.29390600	0.47712700

H	12.46127900	-2.55736600	1.16365600
C	14.42219200	-0.05681100	-0.08416900
H	13.66054000	1.79370500	-0.90931300
H	14.84559300	-2.00752700	0.72406000
C	10.00877400	-1.49300000	1.93950700
C	10.48043000	-0.83425300	3.08294500
C	9.23614300	-2.65582500	2.08539800
C	10.17112700	-1.31758900	4.35342500
H	11.10003300	0.05097400	2.97440700
C	8.92995400	-3.13987900	3.35381900
H	8.88711900	-3.18265800	1.20228700
C	9.37358400	-2.46575400	4.50401000
H	10.56466100	-0.81088400	5.22984800
H	8.34421100	-4.04781500	3.46647900
C	9.37751300	-0.86084700	-0.35134000
C	8.03429000	-0.58917600	-0.00681000
C	9.71597900	-0.97447800	-1.71730500
C	7.06080200	-0.45240500	-0.98762300
H	7.75464100	-0.48433100	1.03522300
C	8.75098100	-0.81559700	-2.70509000
H	10.74010300	-1.18088300	-2.00621000
C	7.43162800	-0.56733100	-2.32773000
H	6.03215900	-0.24292000	-0.71284300
H	9.02917700	-0.88753700	-3.75262700
N	6.39394000	-0.40095500	-3.34212100
C	5.44631900	0.70313900	-3.34997100
C	4.11614300	0.52371900	-2.95554500
H	5.87654600	1.64321900	-3.67227800
C	3.58487000	-0.71625200	-2.48116700
C	3.23274800	1.64841900	-3.00591200
C	2.26610000	-0.81198300	-2.08741500
H	4.21770100	-1.59703300	-2.42771400
C	1.91741500	1.53246500	-2.60985600
H	3.61359900	2.60570300	-3.35034300
C	1.38918800	0.30209100	-2.13943300
H	1.89197500	-1.77453100	-1.75406600
H	1.28466300	2.41366900	-2.63631200
C	-0.01598500	0.18988300	-1.71774800
C	-0.41262200	-0.73241100	-0.72554500
C	-1.01756600	1.00052600	-2.29497900
C	-1.74034100	-0.82795900	-0.32318900
H	0.32828500	-1.35897500	-0.23826300
C	-2.34184600	0.90614600	-1.88595600
H	-0.76496900	1.68929300	-3.09554200

C	-2.73067300	0.00372300	-0.87798600
H	-2.01378800	-1.54019700	0.45035300
H	-3.09270400	1.53444300	-2.35496100
C	-4.14747900	-0.10093900	-0.43789200
C	-4.90597200	1.00081100	-0.14890200
C	-4.68319200	-1.48660200	-0.32946700
C	-6.38270500	0.92732700	0.02351400
C	-4.30733800	2.35325500	0.02114200
C	-5.37449500	-1.91276800	0.81799700
C	-4.48470500	-2.41830700	-1.36291300
C	-7.19370800	0.25183700	-0.90548700
C	-7.01275900	1.56413800	1.10684100
C	-3.18218300	2.55428800	0.83976800
C	-4.87180300	3.47537000	-0.61000600
C	-5.87548400	-3.20790500	0.91512200
H	-5.51526500	-1.21948700	1.64195400
C	-4.99364900	-3.71207700	-1.27164600
H	-3.94646800	-2.11721200	-2.25785100
C	-8.57459300	0.18887500	-0.74169500
H	-6.73373300	-0.22242000	-1.76728000
C	-8.39342400	1.49287100	1.27826200
H	-6.41047800	2.10133100	1.83462900
C	-2.62280700	3.81965300	0.99413400
H	-2.74793500	1.70797000	1.36377200
C	-4.30691600	4.74045000	-0.46541500
H	-5.74836800	3.34924200	-1.23989400
C	-5.70522200	-4.13290800	-0.13246300
H	-6.38428700	-3.51172900	1.82582500
H	-4.85857000	-4.39414700	-2.10658500
C	-9.20386100	0.79927700	0.35994200
H	-9.17388900	-0.31929100	-1.49214300
H	-8.84343900	1.96150100	2.14906700
C	-3.16639100	4.93887200	0.33567100
H	-1.76876700	3.94394400	1.65418900
H	-4.74274000	5.57905900	-1.00137200
C	-6.25584900	-5.50634300	-0.03595300
C	-10.67313000	0.71867900	0.54265400
C	-2.55883000	6.28321800	0.48494500
C	-7.49530500	-5.74597100	0.58441800
C	-5.55413700	-6.61056500	-0.56505700
C	-11.38083000	-0.45036200	0.20928500
C	-11.40242600	1.81191900	1.05713200
C	-3.36194100	7.44225300	0.54346800
C	-1.16357300	6.44031400	0.56974700

C	-8.01225700	-7.03768500	0.67287500
H	-8.07077600	-4.91404800	0.98016300
C	-6.06939900	-7.89871000	-0.47791200
H	-4.58366700	-6.45696400	-1.02858800
C	-12.76234600	-0.52307600	0.38233100
H	-10.84509000	-1.31748600	-0.16627900
C	-12.77978400	1.73996100	1.23006500
H	-10.88425900	2.73506600	1.30111600
C	-2.79442600	8.70387900	0.67992900
H	-4.44353600	7.34783200	0.50467100
C	-0.59384600	7.70530600	0.70690500
H	-0.51726800	5.56968900	0.50458600
C	-7.30970300	-8.13256000	0.14389100
H	-8.97671500	-7.19674000	1.15026800
H	-5.51283800	-8.73839600	-0.88276100
C	-13.48277400	0.56826400	0.89449500
H	-13.28651800	-1.44090600	0.12490600
H	-13.32663400	2.59372300	1.61811500
C	-1.39806000	8.85520000	0.76290100
H	-3.42669400	9.58485100	0.73247500
H	0.48826000	7.80212400	0.76183300
C	-7.88882600	-9.48250500	0.25515300
C	-14.94180000	0.45400300	1.06351700
C	-0.76023200	10.17558300	0.90473200
H	-8.86329500	-9.52521200	0.76040300
H	-15.36584100	-0.51400300	0.76379600
H	0.33681300	10.15423100	0.95861700
N	-1.42337900	11.27274700	0.96149000
H	-0.78740100	12.06756800	1.06009200
N	-15.67207000	1.40366900	1.52366900
H	-16.65218200	1.11357700	1.55716900
N	-7.31041200	-10.53446500	-0.19835200
H	-7.88339000	-11.36159400	-0.01526500
N	9.04203500	-3.01730800	5.76453000
N	15.79540000	0.19307500	-0.31889700
C	8.72688300	-2.24557300	6.73092500
H	8.64760100	-1.15485300	6.63827800
H	8.51173300	-2.68277300	7.70560700
C	16.27465700	1.35497800	-0.09762600
H	17.32490600	1.54271000	-0.31941900
H	15.68995000	2.18571300	0.31769800
C	6.29324900	-1.14694600	-4.36719600
O	6.16910200	-1.79668100	-5.31073000

Sum of electronic and thermal Free Energies = -3348.603140 (Hartree/Particle).

From TDDFT calculation in acetonitrile, λ_{abs} = 529.46 nm.

Table-S16. DFT-optimized geometry of **[TPA-TPE-CO]** (singlet), computed at the B3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	6.08291000	-1.08656900	1.86146500
C	6.77543700	-1.81309300	2.86427700
C	8.16433300	-1.66562900	3.01379700
C	6.09509300	-2.71110600	3.70535300
C	8.85423000	-2.38428200	3.98774100
H	8.70506300	-0.99211000	2.35557000
C	6.78665800	-3.43141300	4.67474400
H	5.02461500	-2.84903800	3.58912400
C	8.17060400	-3.26299800	4.84736600
H	9.93180700	-2.27270600	4.06863700
H	6.25773900	-4.13481500	5.31210800
C	4.78875200	-0.56252100	2.11423200
C	4.48705100	0.02448400	3.35492800
C	3.77819800	-0.63457400	1.13743100
C	3.21293000	0.52496900	3.61428700
H	5.25196800	0.07504700	4.12381300
C	2.50557600	-0.13642900	1.39992400
H	3.98950900	-1.09054900	0.17504000
C	2.20671000	0.46360900	2.63389900
H	2.99529300	0.94832800	4.59091000
H	1.72767500	-0.20922200	0.64575800
C	6.63855300	-0.97763500	0.55868400
C	6.58200200	0.24453700	-0.13107500
C	7.22450200	-2.08913200	-0.06816900
C	7.05658200	0.34217800	-1.43493900
H	6.14234300	1.11161700	0.35211000
C	7.70584000	-1.99581000	-1.37303500
H	7.27879800	-3.03630600	0.45947600
C	7.60117400	-0.78328600	-2.06611500
H	6.98610100	1.28075300	-1.97589800

H	8.12476000	-2.86827100	-1.86505000
N	7.96819500	-0.68055800	-3.43122300
C	7.01053300	-0.36391300	-4.62655700
C	5.55151600	-0.42113600	-4.34016300
H	7.36246800	0.48736900	-5.20492200
C	4.91863600	-1.61187900	-3.94778100
C	4.81449400	0.77174300	-4.30756500
C	3.59838800	-1.60186800	-3.50538800
H	5.45958400	-2.55372400	-3.97948600
C	3.49524700	0.78134000	-3.85865900
H	5.29035800	1.70624600	-4.59503700
C	2.86494600	-0.40239700	-3.43046600
H	3.13170400	-2.54008300	-3.22006600
H	2.96681400	1.72819900	-3.79789900
C	1.48661400	-0.37494000	-2.88301300
C	1.09906600	-1.24893200	-1.84959700
C	0.53100000	0.54456400	-3.35476000
C	-0.17696500	-1.18704900	-1.29377400
H	1.81371900	-1.96104600	-1.44664300
C	-0.73803500	0.61573300	-2.78749500
H	0.77615100	1.20380000	-4.18275500
C	-1.10946100	-0.23104900	-1.72903100
H	-0.44127700	-1.86208300	-0.48396700
H	-1.45413300	1.34056700	-3.16325500
C	-2.45505400	-0.12519800	-1.09815200
C	-2.94969900	1.07569700	-0.67080100
C	-3.20472300	-1.40315900	-0.96028800
C	-4.37506700	1.27251100	-0.29217100
C	-2.07666800	2.27735000	-0.54810500
C	-3.82919800	-1.75670000	0.24908100
C	-3.27477900	-2.31556700	-2.02750500
C	-5.42034600	0.79766800	-1.10418600
C	-4.71776700	1.97387100	0.87713500
C	-0.86258900	2.21257900	0.15594300
C	-2.45158900	3.51118200	-1.10627100
C	-4.52212400	-2.95725900	0.37637600
H	-3.76242000	-1.08316500	1.09829300
C	-3.97538000	-3.51361900	-1.90490500
H	-2.79233900	-2.07234900	-2.97049200
C	-6.75205100	0.98805500	-0.74640100
H	-5.18193600	0.27953200	-2.02830300
C	-6.04984900	2.15712400	1.24170900
H	-3.92971700	2.35984400	1.51828500
C	-0.03425300	3.32542700	0.26062900

H	-0.56957400	1.28629500	0.63956600
C	-1.61841700	4.62444300	-1.01025400
H	-3.39319300	3.59079100	-1.64359500
C	-4.61845900	-3.85819700	-0.70129600
H	-4.97134100	-3.21032700	1.33285900
H	-4.04317400	-4.17724600	-2.76261300
C	-7.09622400	1.66370400	0.43997700
H	-7.53459100	0.63014800	-1.40989400
H	-6.27806600	2.66829100	2.17294800
C	-0.38659500	4.55231200	-0.33179300
H	0.88434900	3.24411400	0.83463200
H	-1.91701900	5.55219500	-1.49069600
C	-5.36782600	-5.13075500	-0.56921000
C	-8.51464100	1.85349700	0.82800900
C	0.51087500	5.72845200	-0.23457600
C	-6.55692000	-5.19582700	0.17944800
C	-4.91029400	-6.31192700	-1.19157300
C	-9.47192700	0.85224000	0.58334600
C	-8.94429400	3.04275100	1.45494200
C	-0.00790200	7.03335000	-0.09363500
C	1.90864500	5.57413400	-0.27788500
C	-7.26010600	-6.39349400	0.30138600
H	-6.94768600	-4.29861300	0.65093900
C	-5.61110400	-7.50627800	-1.07070500
H	-3.98212200	-6.29562100	-1.75595200
C	-10.80476600	1.03268100	0.95024600
H	-9.16836600	-0.08408500	0.12389300
C	-10.27295100	3.22306400	1.82154200
H	-8.23090500	3.84224600	1.63429100
C	0.83392300	8.13549300	0.00222200
H	-1.08280600	7.17960700	-0.03479800
C	2.75340300	6.67869100	-0.18054200
H	2.33853300	4.58541800	-0.41039600
C	-6.80004800	-7.56561400	-0.32059900
H	-8.18156900	-6.41670300	0.87916000
H	-5.24045700	-8.40781100	-1.54875700
C	-11.22624400	2.21811500	1.57435800
H	-11.52499700	0.24040200	0.75790800
H	-10.58788100	4.14782900	2.29507300
C	2.23119000	7.97467900	-0.03872100
H	0.41860200	9.13176400	0.11954200
H	3.83074900	6.53420500	-0.22357900
C	-7.56997900	-8.81242800	-0.17000200
C	-12.64280700	2.37175200	1.94819000

C	3.15498600	9.11742200	0.06289800
H	-8.48159800	-8.72074100	0.43603600
H	-13.27961300	1.51078500	1.70323400
H	4.22063100	8.85424300	0.01707300
N	2.75905300	10.33095900	0.19589500
H	3.56160600	10.96274600	0.24727900
N	-13.10982500	3.42387100	2.51568500
H	-14.11296600	3.32005400	2.68545000
N	-7.21421000	-9.92578800	-0.70003100
H	-7.88811900	-10.65987500	-0.47023100
N	0.88456700	0.92271000	2.84082300
N	8.81110600	-4.03307100	5.84771200
C	0.67454400	1.99930700	3.49276300
H	1.47380400	2.64284700	3.88257000
H	-0.35313900	2.31857000	3.66396600
C	9.76935600	-3.52961300	6.52481100
H	10.27491300	-4.15060400	7.26398000
H	10.11465400	-2.49343900	6.41669700
C	7.86075900	-1.56376300	-4.44019200
O	8.18158200	-2.68570400	-4.77752000

Sum of electronic and thermal Free Energies = -3348.815213 (Hartree/Particle).

Table-S17. 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	1.16929200
O	0.00000000	0.00000000	-1.16929200

Sum of electronic and thermal Free Energies = -188.602658 (Hartree/Particle).

Table-S18. 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	0.48738100

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

Table-S19. 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	0.11854000
H	0.00000000	0.76855000	-0.47415900
H	0.00000000	-0.76855000	-0.47415900

Sum of electronic and thermal Free Energies = -76.427699 (Hartree/Particle).

Table-S20. DFT-optimized geometry of **TEA** (singlet), computed at the B3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	-0.00023300	0.00003900	-0.00909700
C	1.13109000	0.83164500	0.43556200
C	1.33749400	2.08095400	-0.42377700
H	2.04065900	0.22556900	0.38408900
H	1.00815300	1.11610700	1.49966700
H	2.19525500	2.65579400	-0.05348200
H	1.53227500	1.79936100	-1.46515700
H	0.46449000	2.74308500	-0.40964800
C	-1.28637800	0.56426300	0.43447900
C	-2.47174800	0.11632700	-0.42360900
H	-1.21667000	1.65495800	0.38073400

H	-1.47107000	0.31763100	1.49910500
H	-3.39821600	0.57298900	-0.05427900
H	-2.32557600	0.42313400	-1.46584600
H	-2.60905900	-0.97069500	-0.40667200
C	0.15390000	-1.39587500	0.43429300
C	1.13579000	-2.19738100	-0.42324800
H	-0.82531000	-1.88108800	0.37911100
H	0.45853900	-1.43286900	1.49926900
H	1.20202900	-3.22891900	-0.05603300
H	0.79911200	-2.22133700	-1.46623100
H	2.14613300	-1.77359800	-0.40315000

Sum of electronic and thermal Free Energies = -292.271473 (Hartree/Particle).

Table-S21. DFT-optimized geometry of **TEA**$^{\cdot+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	-0.00186100	0.00201400	-0.62214400
C	0.59329800	-1.32717100	-0.61226200
H	1.66445300	-1.22192400	-0.78892500
H	0.14952500	-1.87841400	-1.45113600
C	0.85234000	1.18179600	-0.60790100
H	0.22592900	2.05924300	-0.77506500
H	1.54822600	1.07833800	-1.45032100
C	-1.45041200	0.15189600	-0.61005100
H	-1.89667600	-0.82718700	-0.78945000
H	-1.70656100	0.81563800	-1.44552600
C	1.64255300	1.30680700	0.70997900
H	2.30272600	0.44981600	0.86874100
H	2.25844100	2.20826700	0.64325300
H	0.96620600	1.40322400	1.56314400
C	0.31881900	-2.07355700	0.70878300
H	-0.75166500	-2.22046600	0.87483600
H	0.79420900	-3.05617900	0.63989600
H	0.74470600	-1.53422200	1.55864200
C	-1.95598400	0.75907600	0.71403300
H	-1.54115700	1.75585200	0.88512200

H	-3.04423100	0.84548600	0.64567500
H	-1.70479700	0.11535100	1.56063600

Sum of electronic and thermal Free Energies = -292.079251 (Hartree/Particle).

Table-S22. DFT-optimized geometry of **[Et_2N=$CHCH_3$]**· (doublet), computed at the UB3LYP-D3/ 6-31+G* level in acetonitrile solvent using PCM.

Atom	x	y	z
N	-0.04867700	-0.09736800	-0.20868800
C	1.28759600	-0.56254200	-0.60277300
H	1.87125100	0.30317500	-0.93006100
H	1.20141900	-1.23082000	-1.47494500
C	-0.34019500	1.31340300	-0.48082500
H	-1.41355700	1.47340200	-0.36218500
H	-0.09978200	1.54724200	-1.53290300
C	-1.06970300	-1.04461300	-0.26117600
C	0.41250500	2.26450800	0.45379600
H	1.49860100	2.14241700	0.37215700
H	0.17319500	3.30510600	0.20271900
H	0.12771000	2.08286000	1.49649700
C	2.02619100	-1.27467900	0.53385600
H	1.45953500	-2.14278200	0.88934500
H	3.00672100	-1.62658700	0.18994100
H	2.17676500	-0.59550400	1.38089500
C	-2.41647900	-0.76405000	0.34249100
H	-2.98969200	0.00262500	-0.19672200
H	-3.01820500	-1.67933000	0.33113100
H	-2.34634800	-0.42417000	1.39294500
H	-0.70636500	-2.06821000	-0.21021100

Sum of electronic and thermal Free Energies = -291.634151 (Hartree/Particle).

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