

Supplementary Information

Coalescing solar-to-chemical and carbon circular economy: Mediated by metal-free porphyrin and triazine-based porous organic polymer under natural sunlight

Neha Saini, Neha Sharma, Deepak Kumar Chauhan, Rishu Khurana, Md Ehesan Ali and Kamalakannan Kailasam*

Advanced Functional Nanomaterials, Institute of Nano Science and Technology (INST), Knowledge city, Sector-81, Manauli, SAS Nagar, 140306 Mohali, Punjab, India.

*Email: kamal@inst.ac.in

Contents:

Synthesis of TPT-CHO

Apparent Quantum Yield calculations

Solar-to-fuel conversion efficiency

Supplementary Figures S1-S24

Supplementary Scheme S1-S2

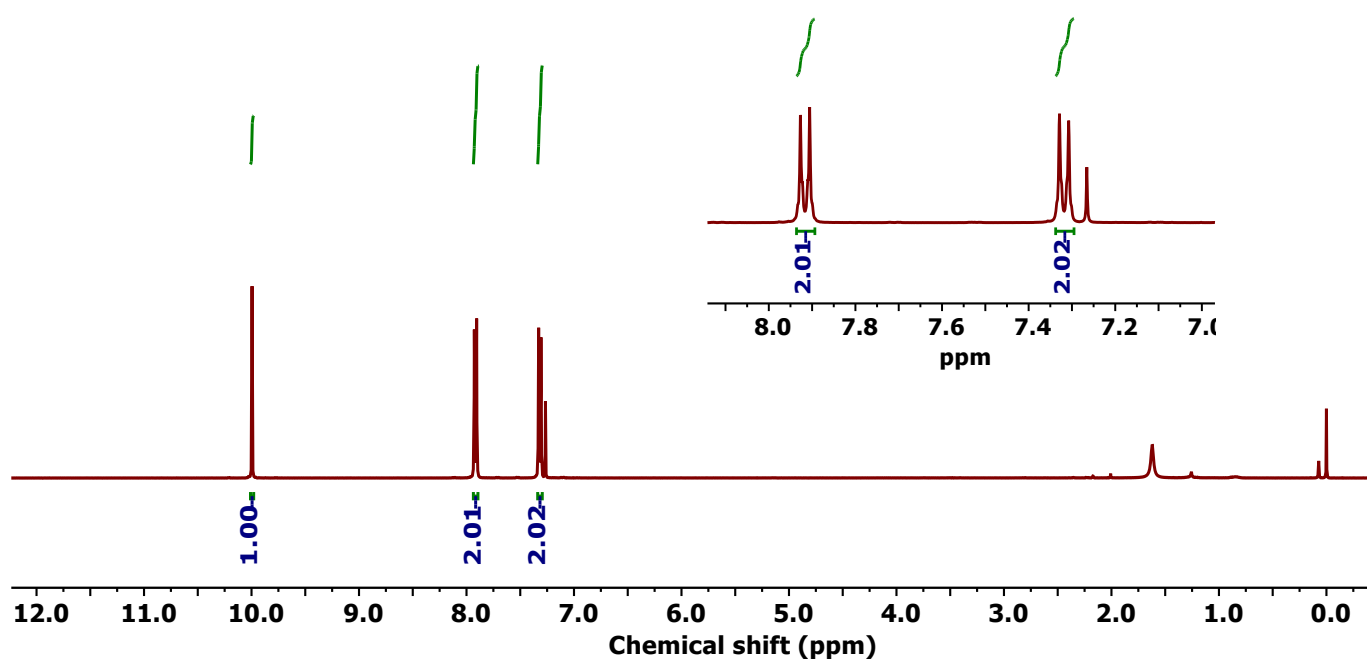
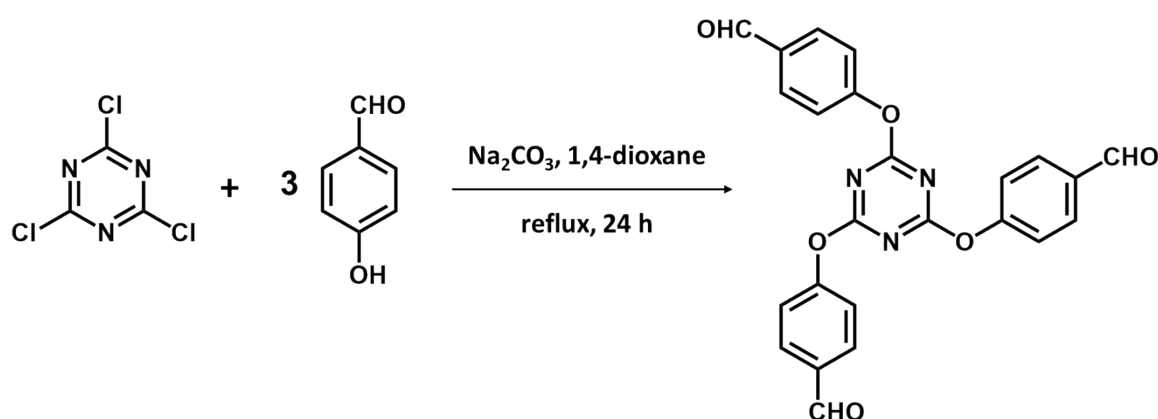
Supplementary Tables S1-S8

Synthesis and Characterization

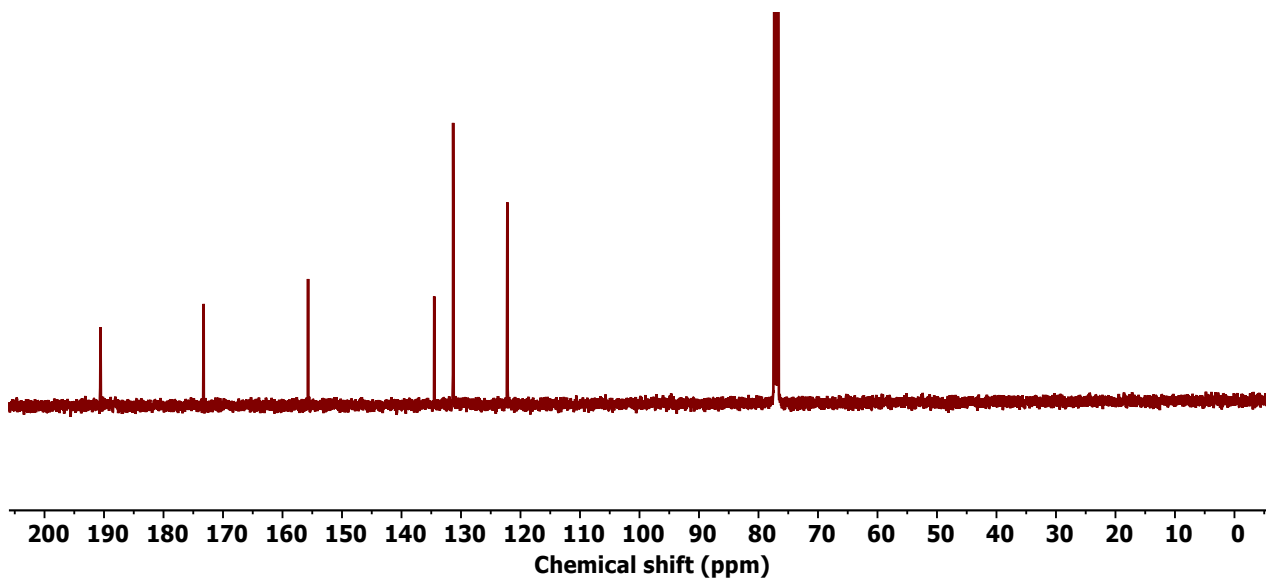
Synthesis of tris- (4-formylphenoxy)-1,3,5-triazine (TPT-CHO)

TPT-CHO was synthesized as per the reported procedure^{1,2} 4-hydroxy benzaldehyde (1.6 g, 13.1 mmol), cyanuric chloride (0.6 g, 3.25 mmol) and sodium carbonate (2.0 g, 18.8 mmol) were suspended into 15 ml of 1,4-dioxane taken in a round bottom flask. This mixture was refluxed for 24 h and then allowed to cool down. The precipitates were filtered out and washed with 10% aqueous Na₂CO₃ solution and distilled water. The white solid product was recrystallized with ethyl acetate to afford white fluffy precipitates of TPT-CHO which were dried at 70 °C in a vacuum oven.

¹H NMR (CDCl₃, 400 MHz): 9.95 (s, 3H), 7.91 (d, 6H), 7.31 (d, 6H) ppm. ¹³C NMR (CDCl₃, 400 MHz): 190.6, 173.2, 155.7, 134.4, 131.3, 122.2 ppm.



¹H NMR spectra of TPT-CHO in CDCl₃



^{13}C NMR spectra of TPT-CHO in CDCl_3

Apparent Quantum Yield (AQY%) calculations

Apparent Quantum Yield is widely used to calculate the performance of the photocatalyst. It is defined as the number of electrons reacted to the number of incident photons. The apparent quantum yield (AQY) for CO_2 photoreduction reaction was evaluated with 5mg of TPT-porp under light irradiation for 2 h using 400 W Xe lamp with different band-pass filters. Assume that the incident photons are all absorbed by the sample. The AQY was calculated according to the below equation:

$$AQY (\%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100 \quad (1)$$

Since the photoreduction of CO_2 to CO involves two electrons therefore, AQY is given as equation (2)

$$AQY (\%) = \frac{2 \times \text{Number of CO evolved}}{\text{Number of incident photons}} \times 100 \quad (2)$$

Number of incident photons is defined as the ratio of total energy incident to the energy of single photon i.e., eq (3)

$$\text{Number of incident photons} = \frac{E_{total}}{E_{photon}} \quad (3)$$

Total energy incident, E_{total} is given as

$$E_{total} = I \times A \times t \quad (4)$$

I = intensity of incident light (Wcm^{-2})

A = area of irradiation (cm^2)

t = time of irradiation (s)

Energy of one photon (E_{photon}) with wavelength of λ_{inc} is calculated as

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}}} \quad (5)$$

h (Js) is Planck's constant

c (ms^{-1}) is the speed of light

λ_{inc} (m) is the wavelength of monochromatic light

Combining equations (3), (4) and (5)

$$\text{Number of incident photons} = \frac{I \times A \times t \times \lambda_{\text{inc}}}{hc} \quad (6)$$

$$\text{Number of CO evolved} = \eta_{\text{CO}} \times N_A \quad (7)$$

where, η_{CO} is the moles of CO evolved upon irradiation of incident light for 't' time duration

N_A is the Avagadro's number

Using equations (2), (6) and (7)

$$\text{AQY (\%)} = \frac{2 \times \eta_{\text{CO}} \times N_A \times h \times c}{I \times A \times t \times \lambda_{\text{inc}}} \times 100$$

Solar-to-fuel conversion efficiency for CO (STF%)

The solar-to-fuel conversion efficiency of CO was determined by the reaction carried out under natural sunlight. The STF efficiency is calculated using formula,

$$\text{STF efficiency (\%)} = \frac{[\text{Chemical energy produced}]}{[\text{Solar energy input}]}$$
$$\text{STF efficiency (\%)} = \frac{[\Delta G \text{ for CO production (J/mol)}] [\text{CO formed (mol/s)}]}{[\text{Irradiation intensity (W/cm}^2\text{)}] [\text{Irradiation area (cm}^2\text{)}]} \times 100$$

where, ΔG the free energy change for CO_2 to CO is 257 kJ/mol

amount of CO formed in 1 h (with 5 mg of catalyst TPT-porp) under natural sunlight (intensity = 44.65 mW/cm²) with irradiation area of 6.44 cm² is 2.7 x 10⁻⁹ mol/s

$$STF \text{ efficiency (\%)} = \frac{[(2.57 \times 10^5 \text{ (J/mol)})] [2.7 \times 10^{-9} \text{ (mol/s)}]}{[4.46 \times 10^{-2} \text{ (W/cm}^2\text{)}] [6.44 \text{ (cm}^2\text{)}]} \times 100$$

$$STF \text{ efficiency (\%)} = 0.241\%$$

Supplementary Figures

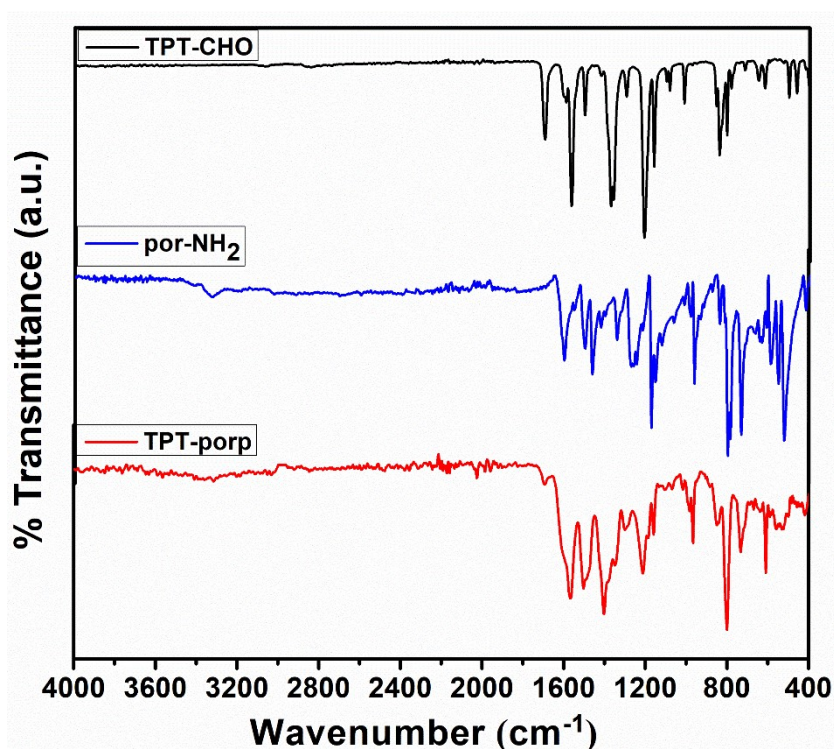
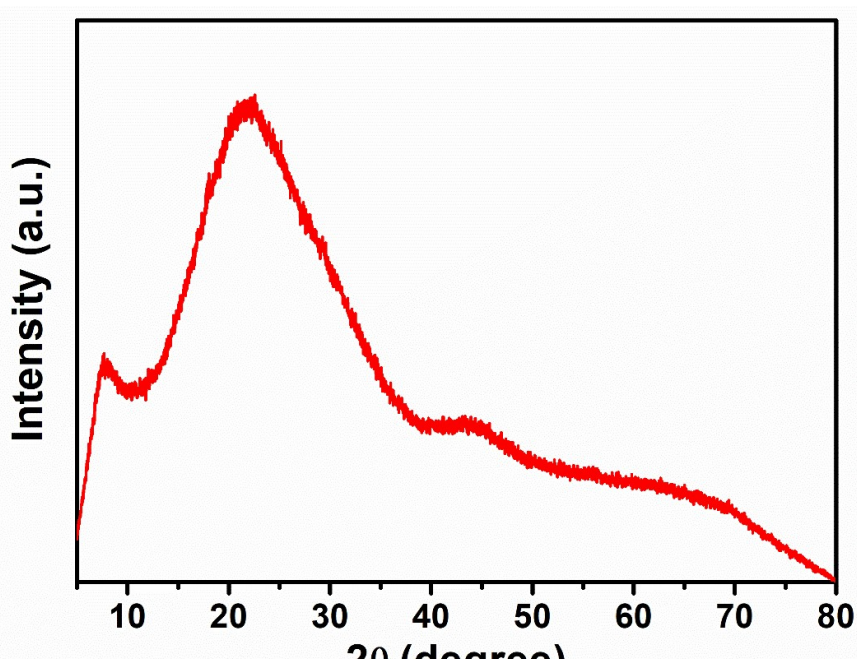


Fig. S1 Comparison of FTIR spectra of TPT-CHO, porp-NH₂, and TPT-porp.



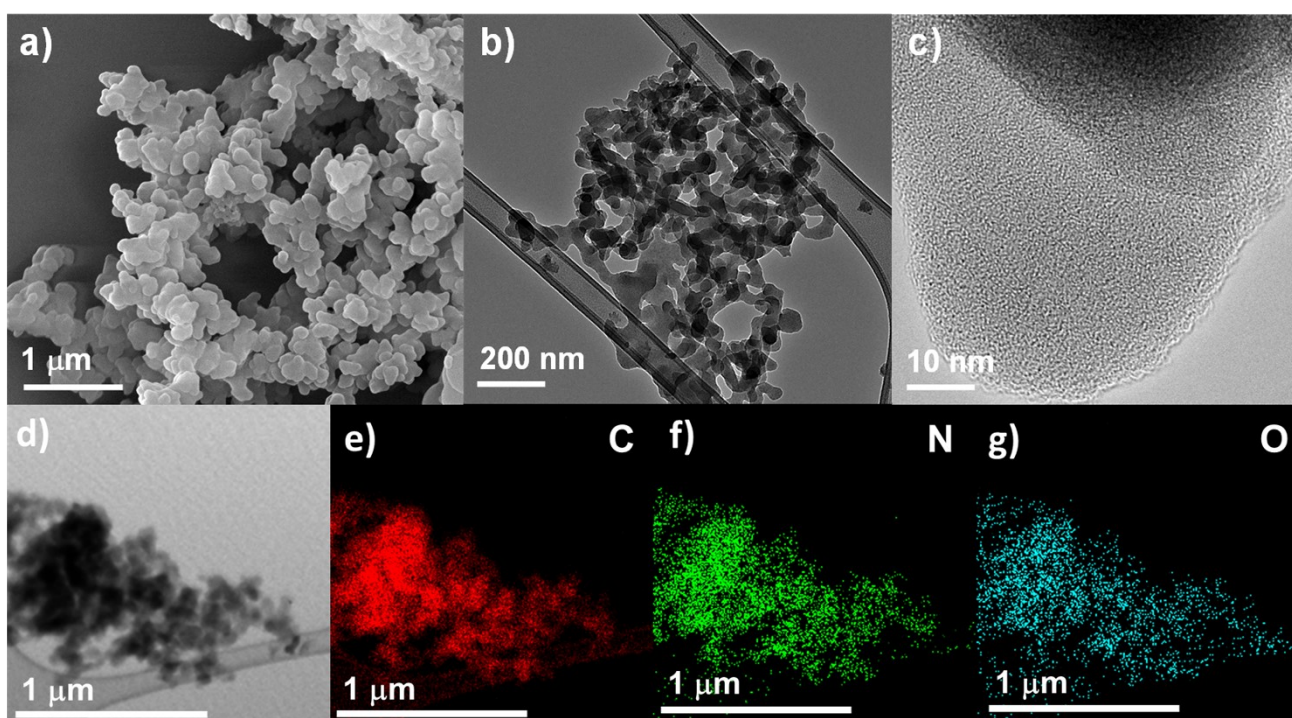


Fig. S3 (a) FESEM images, (b) TEM images, and (d-g) TEM elemental mapping (showing elements C, N and O) of TPT-porp.

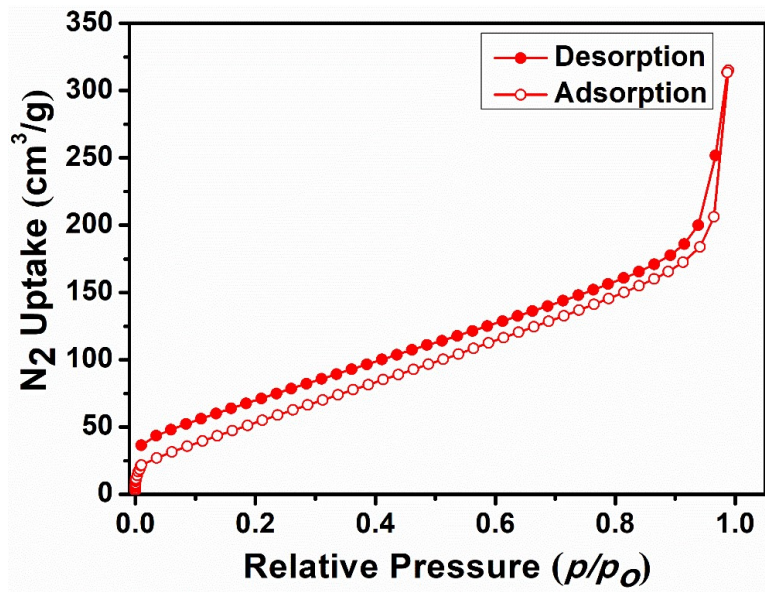


Fig. S4 N₂ adsorption and desorption isotherm of TPT-porp.

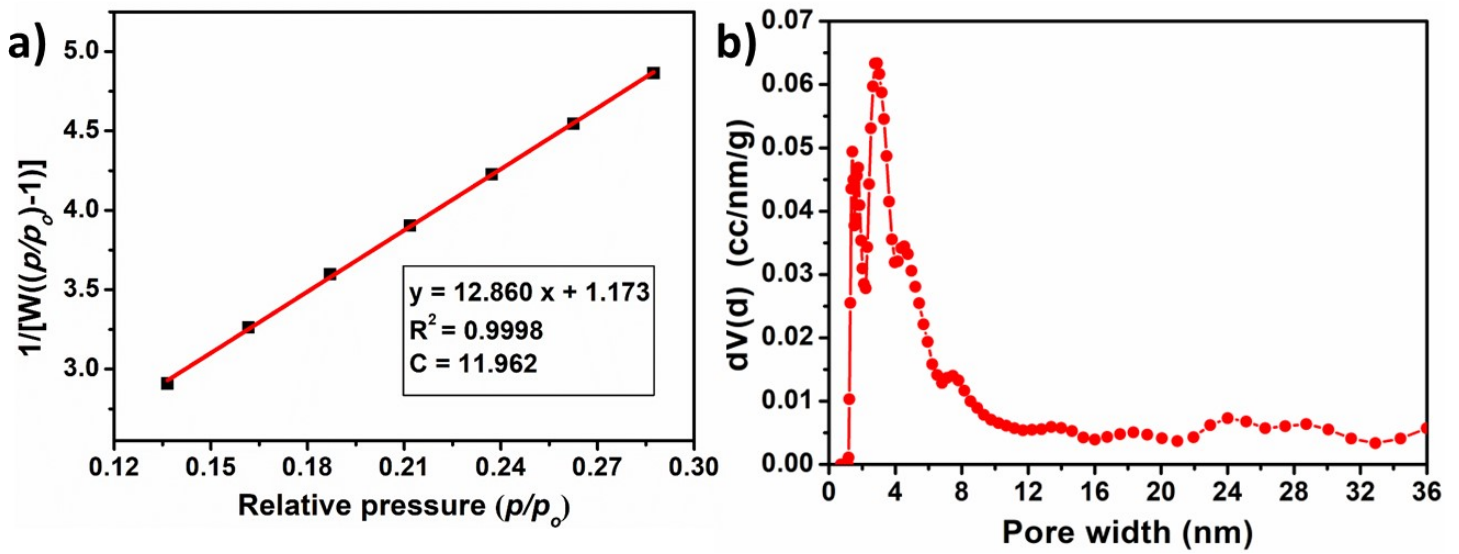


Fig. S5 (a) Linear BET plot and (b) Pore size distribution of TPT-porp.

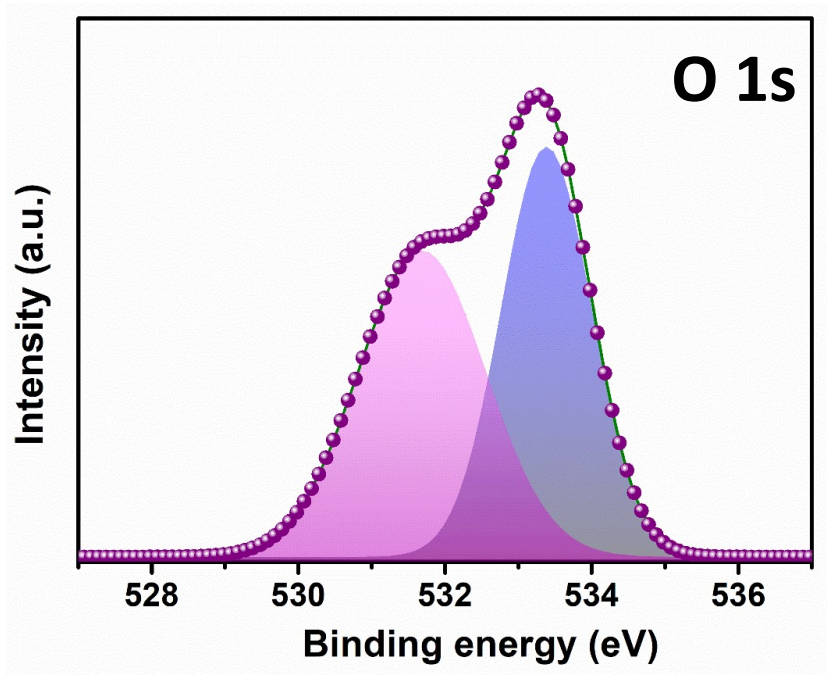


Fig. S6 High-resolution XPS O 1s spectra of TPT-porp.

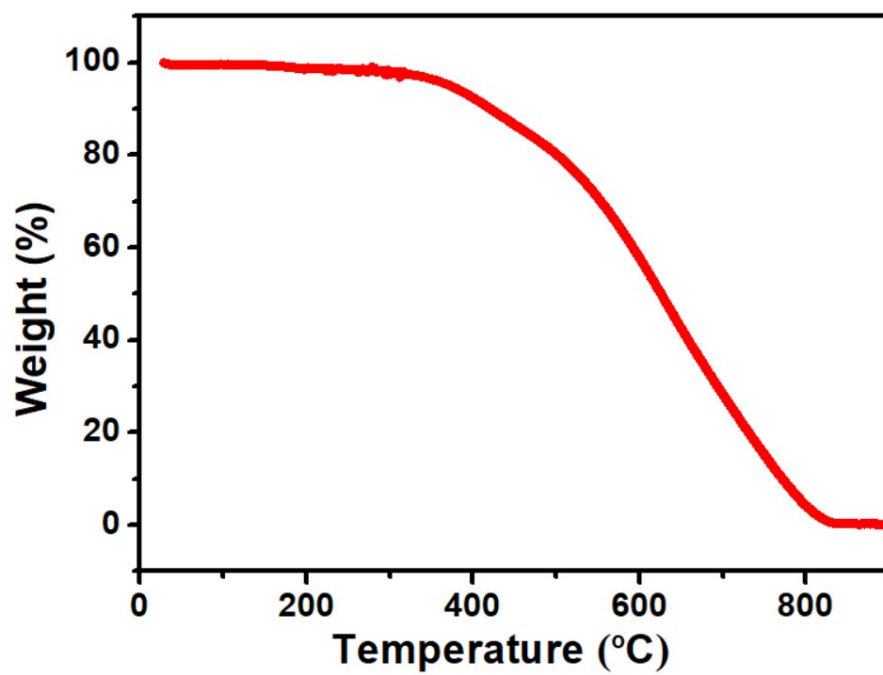


Fig. S7 TGA plot of TPT-porp (under N₂ atmosphere).

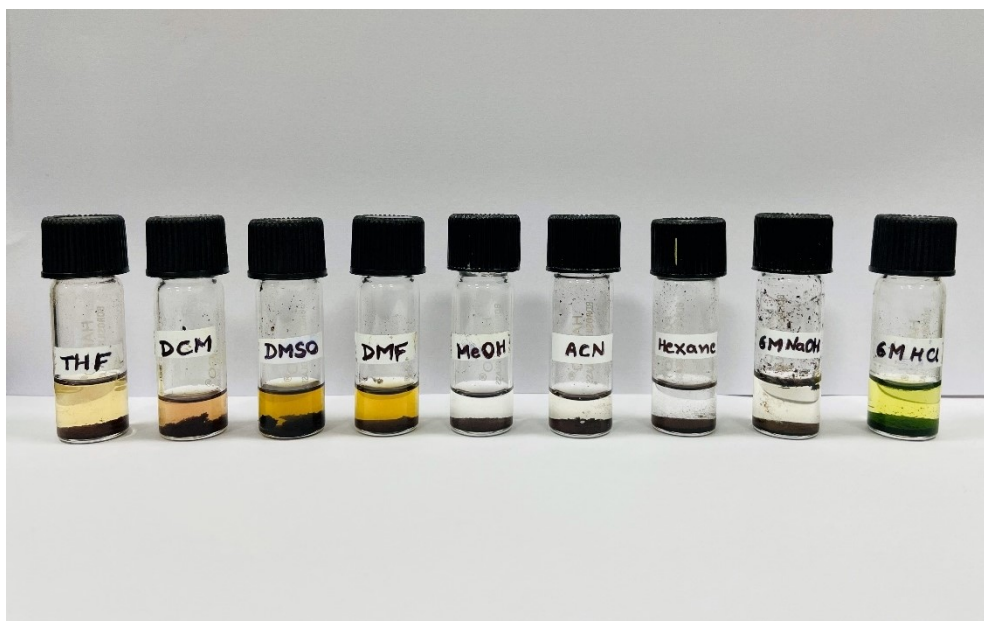


Fig. S8 TPT-porp immersed in various organic solvents, 6 M NaOH and 6 M HCl for 3 days.

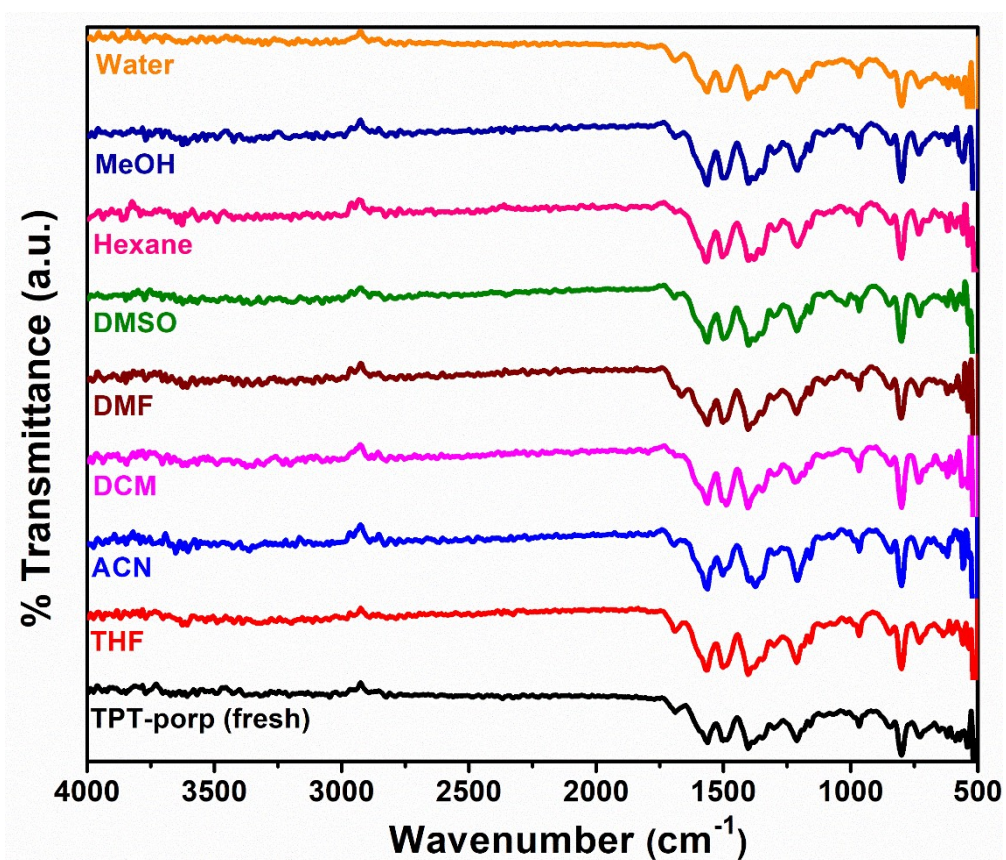


Fig. S9 FTIR spectra of TPT-porp after being immersed into various organic solvents for 3 days.

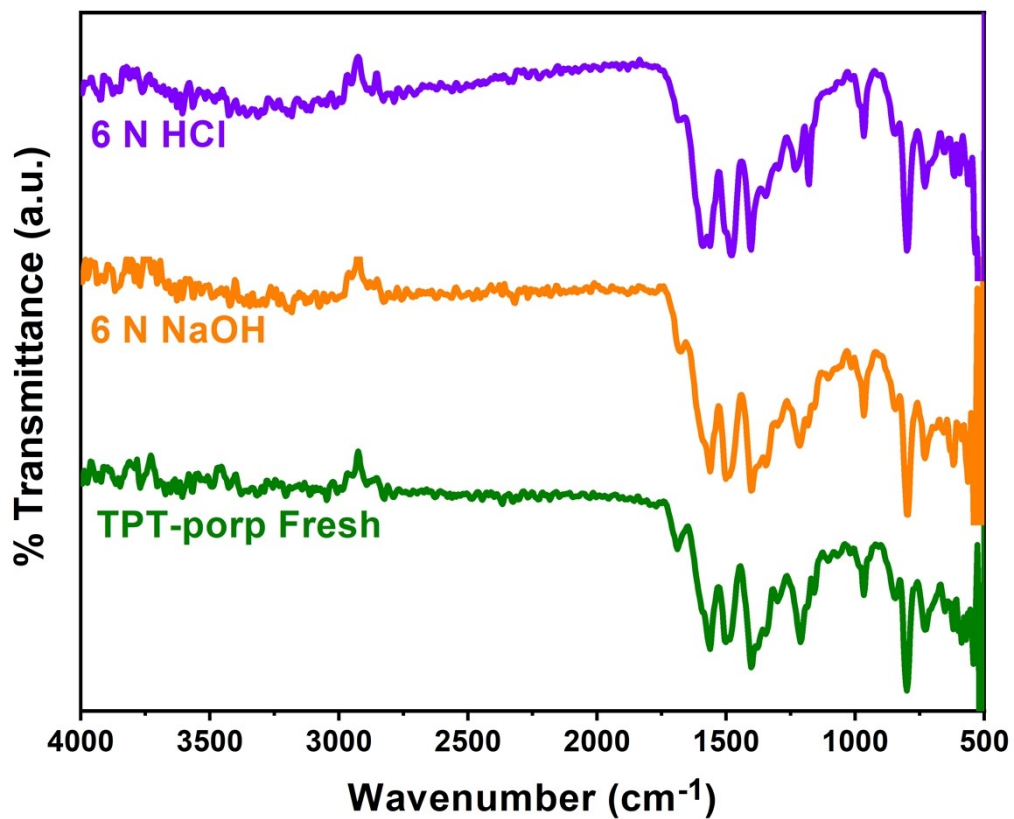


Fig. S10 Comparison of FTIR spectra of TPT-porp after being immersed into 6 N NaOH and 6 N HCl for 3 days.

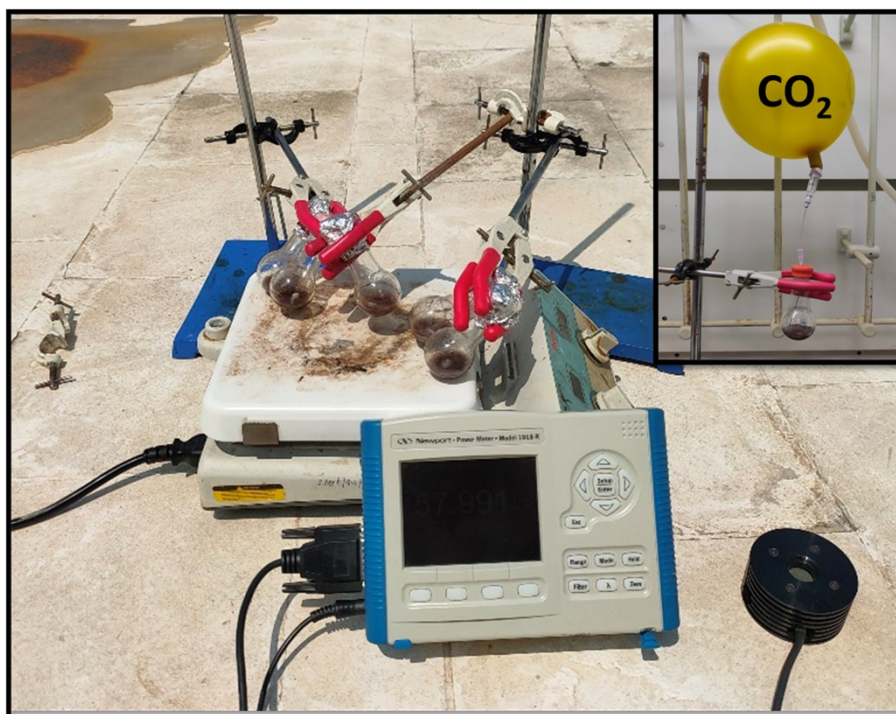


Fig. S11 Photocatalytic reaction setup of simultaneous CO_2 reduction and benzylamine homocoupling under natural sunlight. The inset shows purging of reaction mixture using a CO_2 -filled balloon before irradiation.

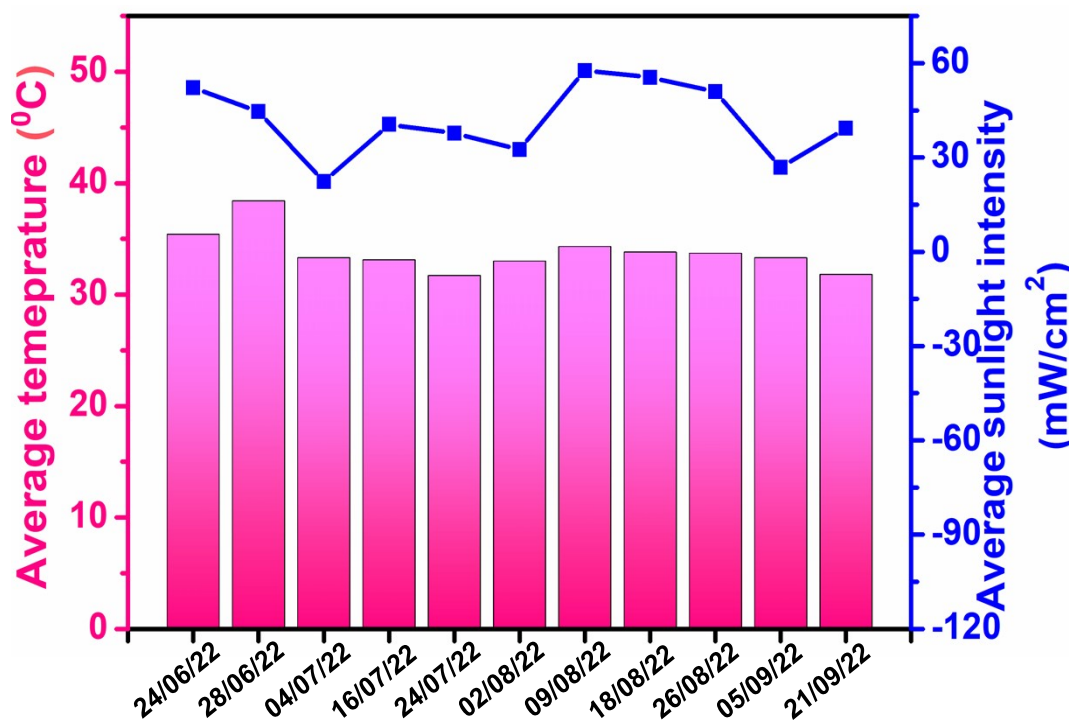


Fig. S12 The average temperature and average solar intensity during this photocatalytic study. The average sunlight intensity was measured by a Newport power meter (Model number: 1918-R).

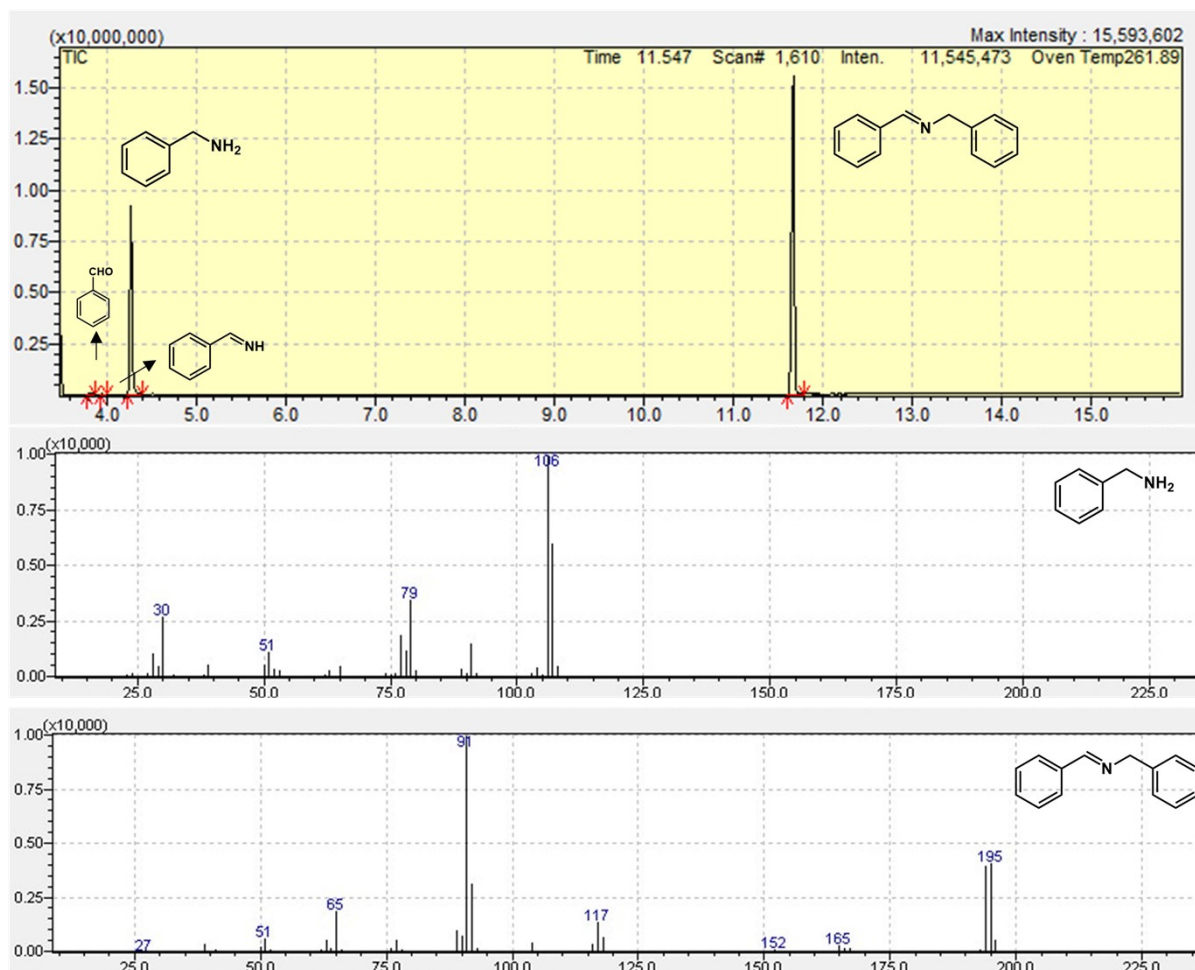


Fig. S13 GC-MS chromatogram for the analysis of liquid product.

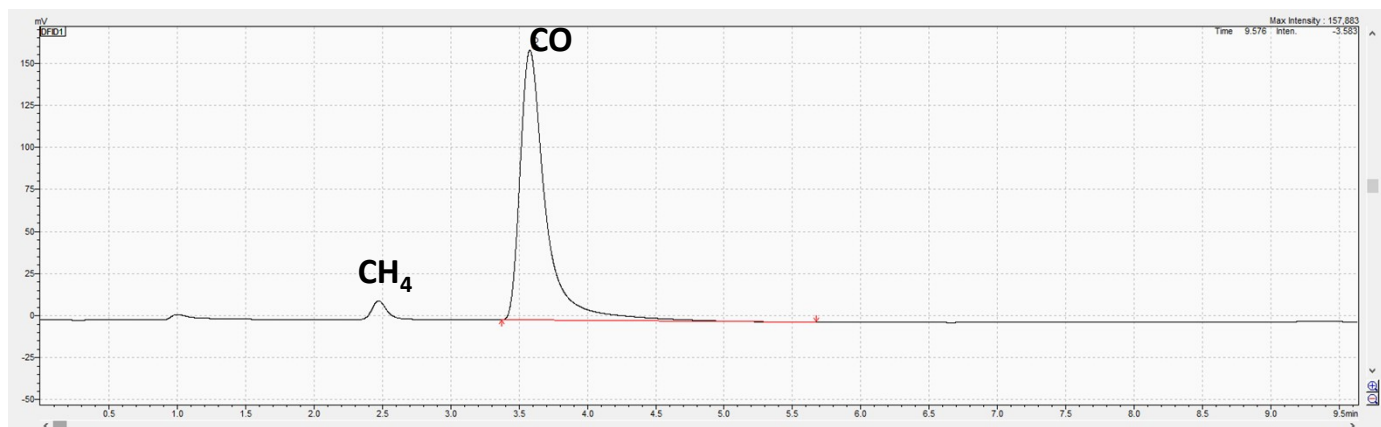


Fig. S14 GC chromatogram for the analysis of gaseous product.

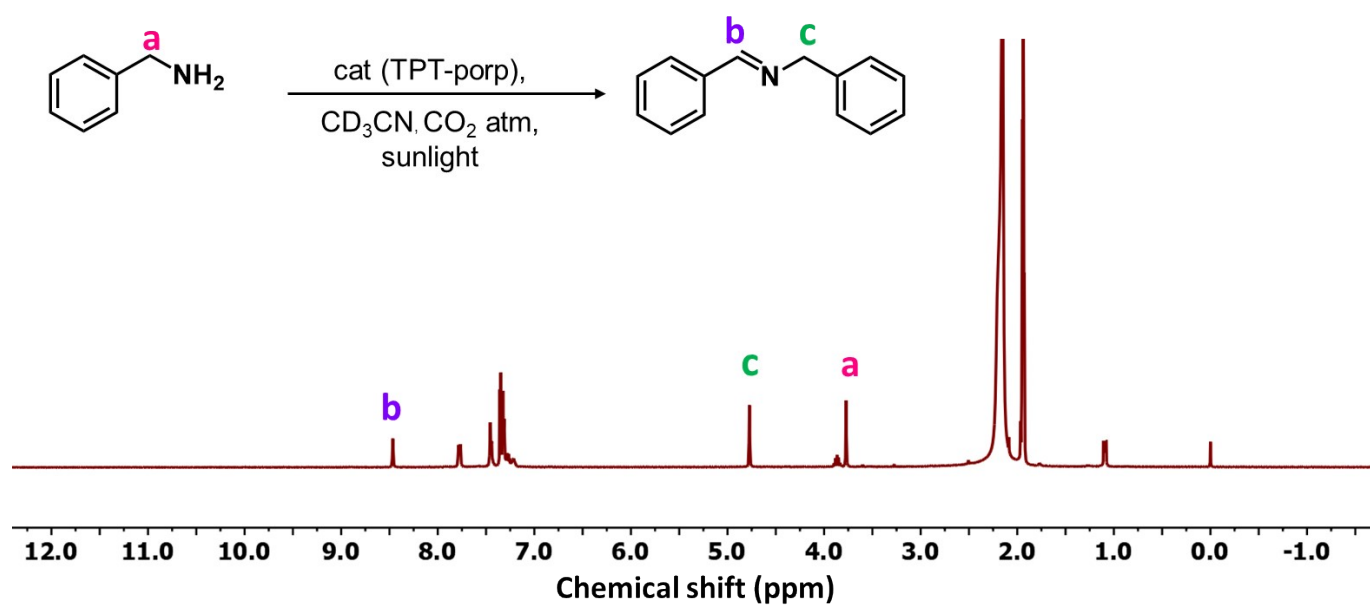


Fig. S15 ^1H NMR of the reaction mixture in deuterated acetonitrile.

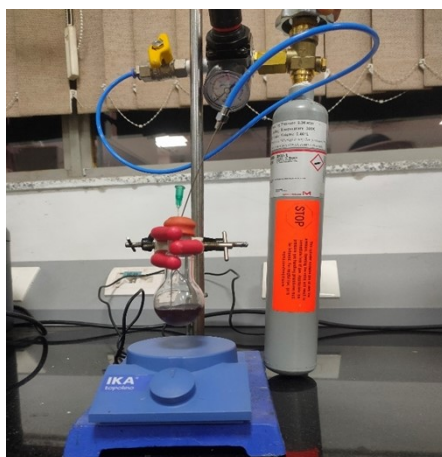


Fig. S16 $^{13}\text{CO}_2$ purging setup for labelling experiments.

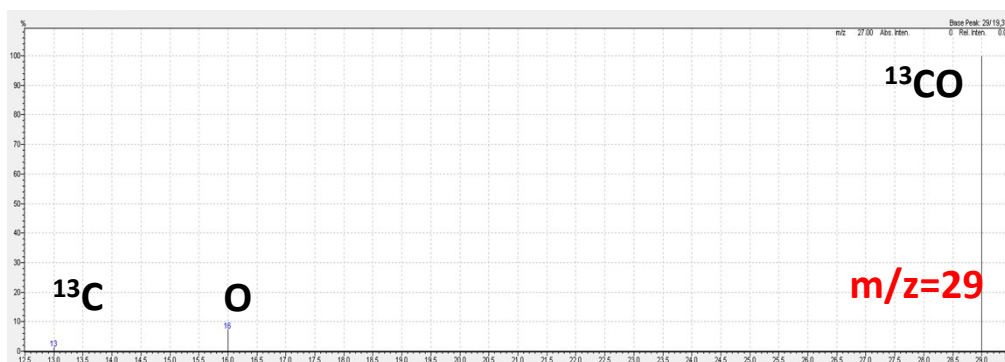


Fig. S17 GC-MS analysis of the generated CO using $^{13}\text{CO}_2$ as feedstock.

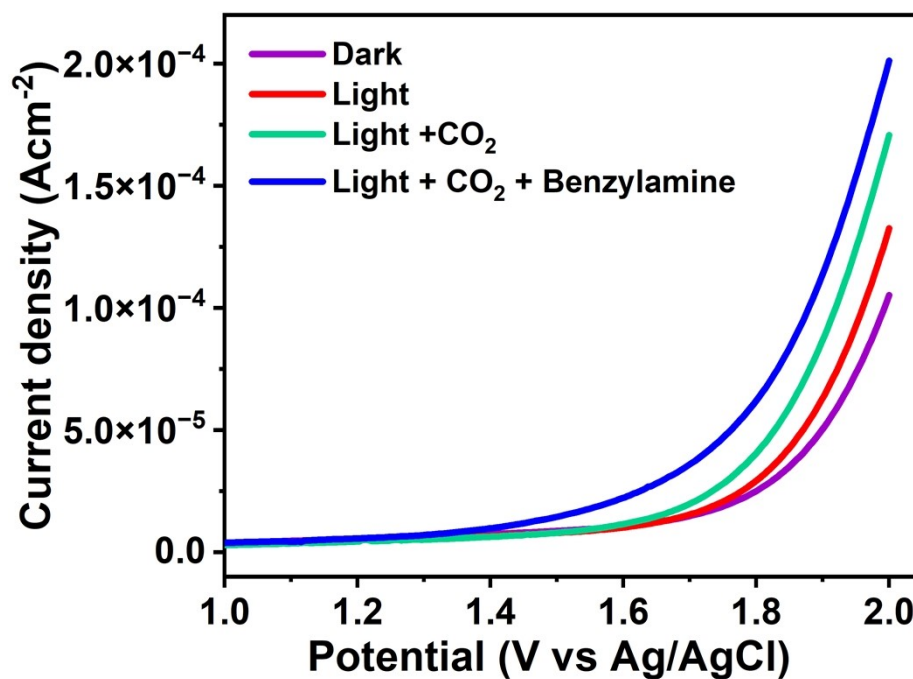


Fig. S18 LSV of TPT-porp without and with addition of benzylamine in presence of CO_2 .

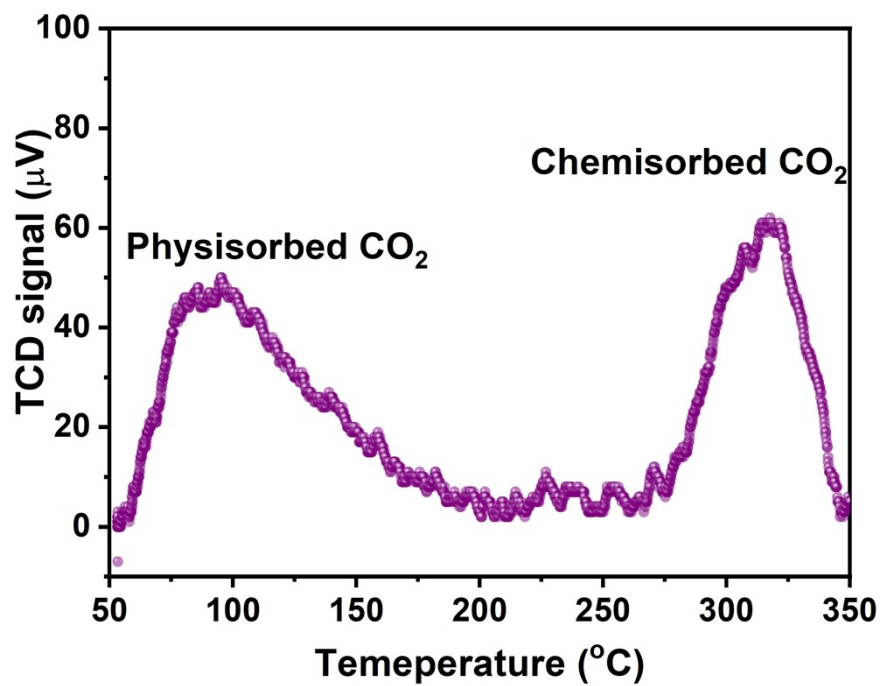


Fig. S19 CO₂-TPD data of TPT-porp.

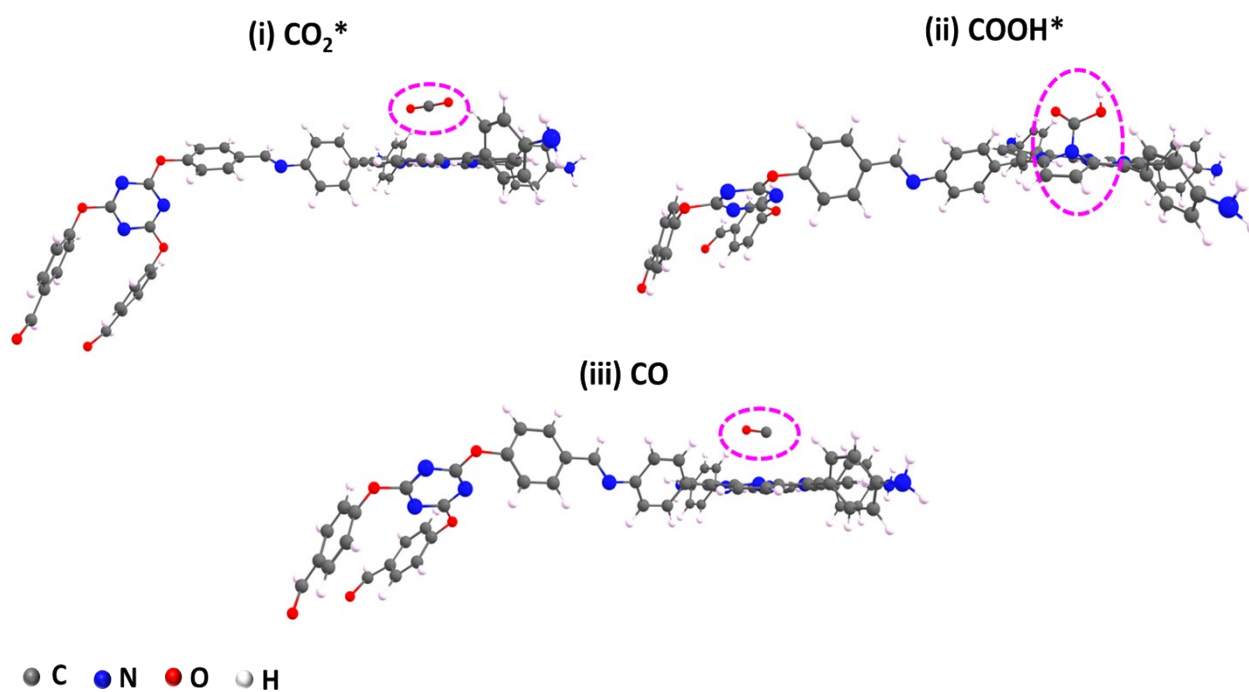


Fig. S20 Steps in Photocatalytic CO₂ reduction; (i) Activation of CO₂, (ii) Formation of COOH intermediate and (iii) Desorption of CO from catalyst surface.

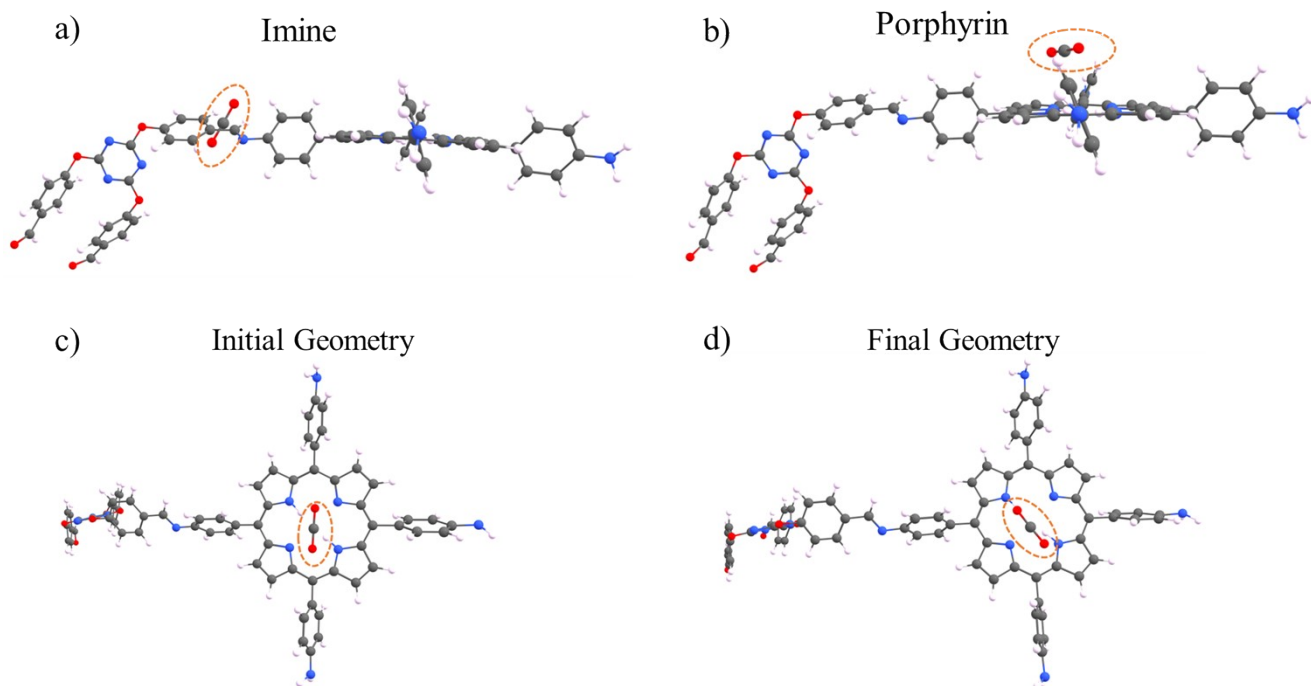


Fig. S21 CO₂ adsorption at (a) Imine and (b) Porphyrin sites; (c) initial and (d) final optimized geometries for adsorption of CO₂ molecule at porphyrin sites.

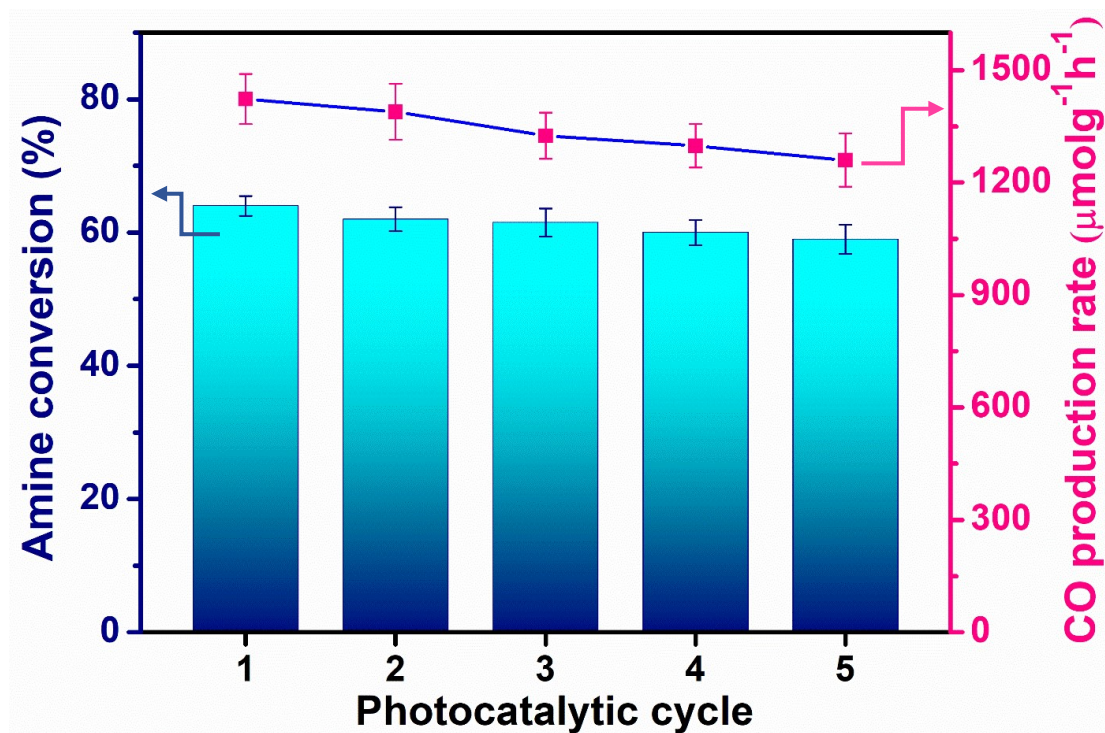


Fig. S22 Photocatalytic performance of TPT-porp under 5 catalytic cycles.

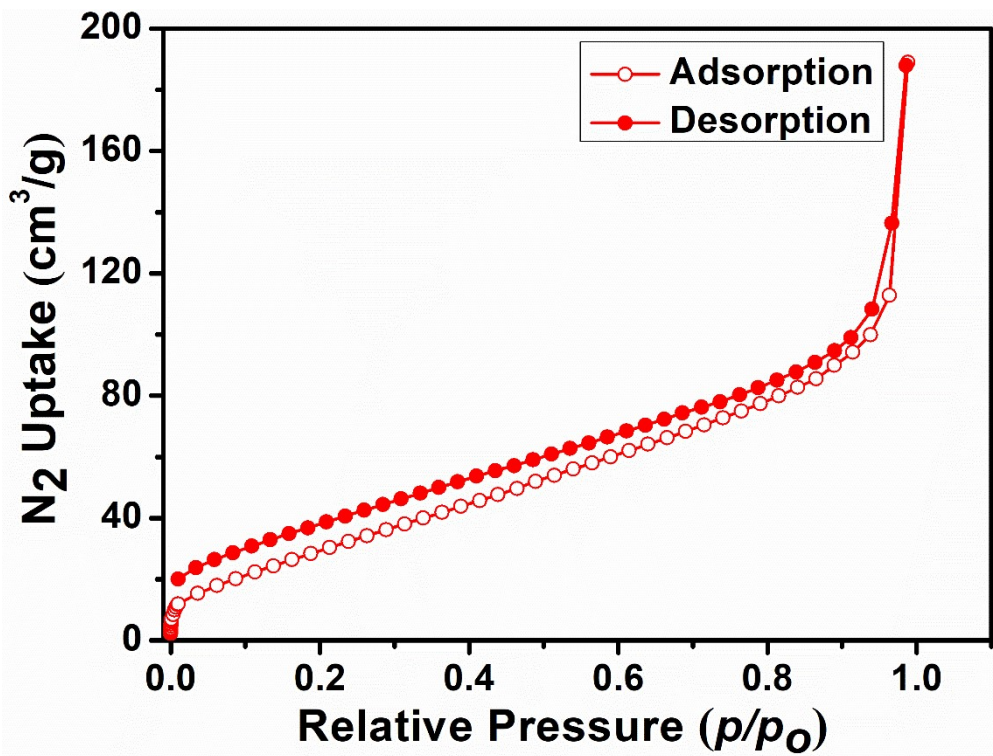


Fig. S23 N₂ sorption isotherm of TPT-porp after recyclability.

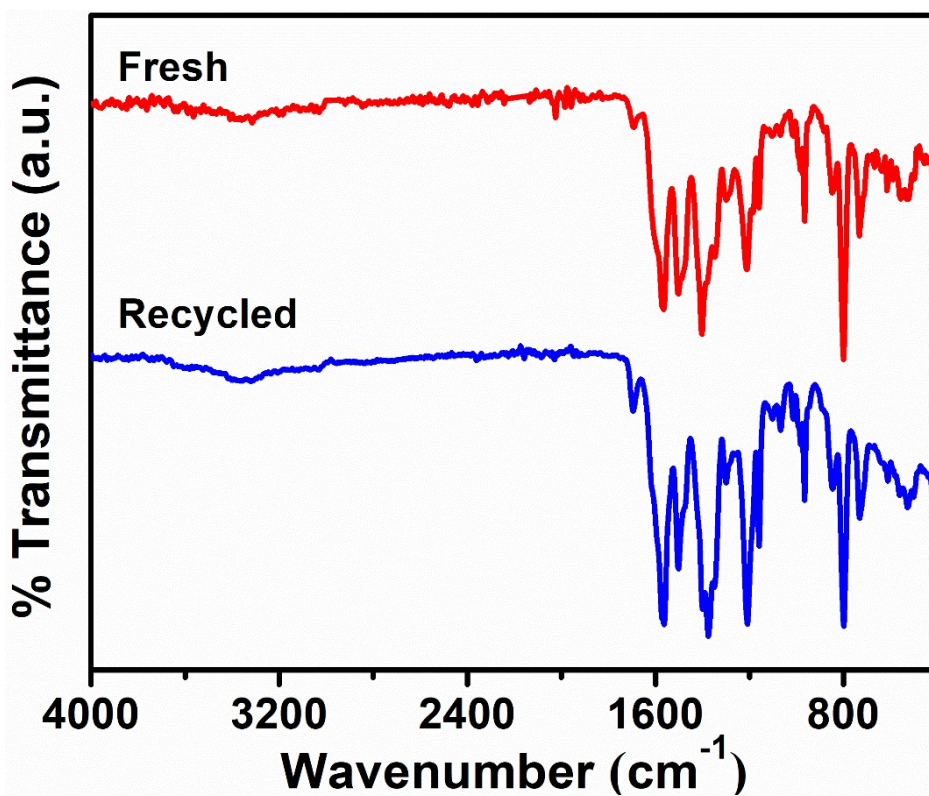


Fig. S24 FTIR spectra of fresh and recycled TPT-porp.

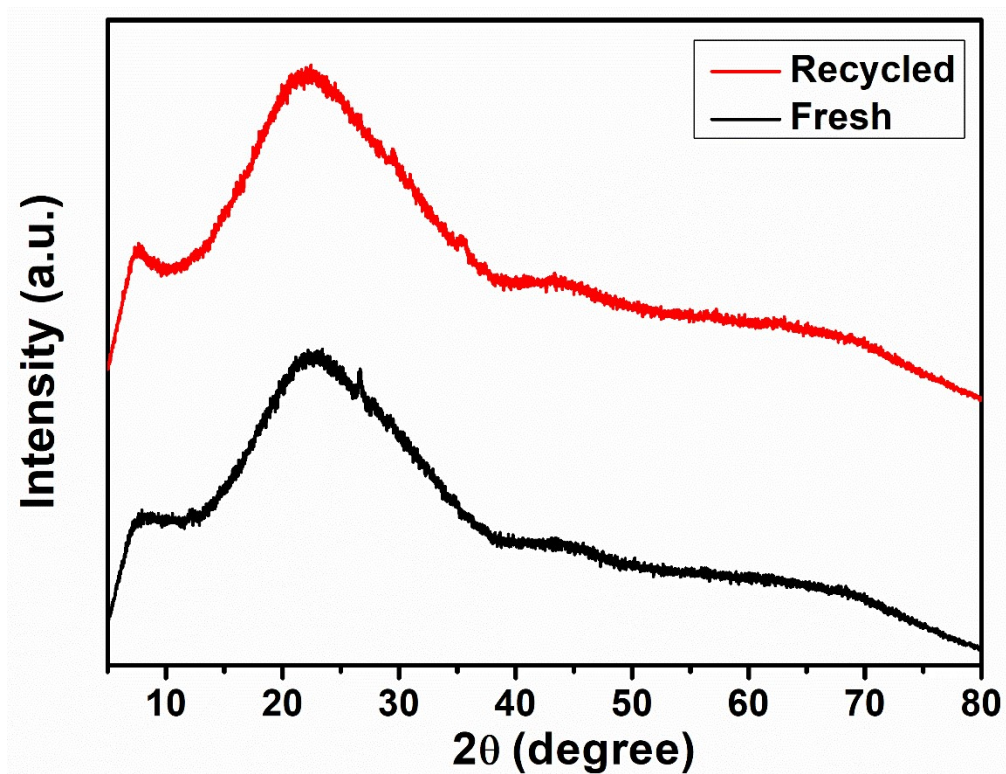


Fig. S25 PXR D spectra of fresh and recycled TPT-porp.

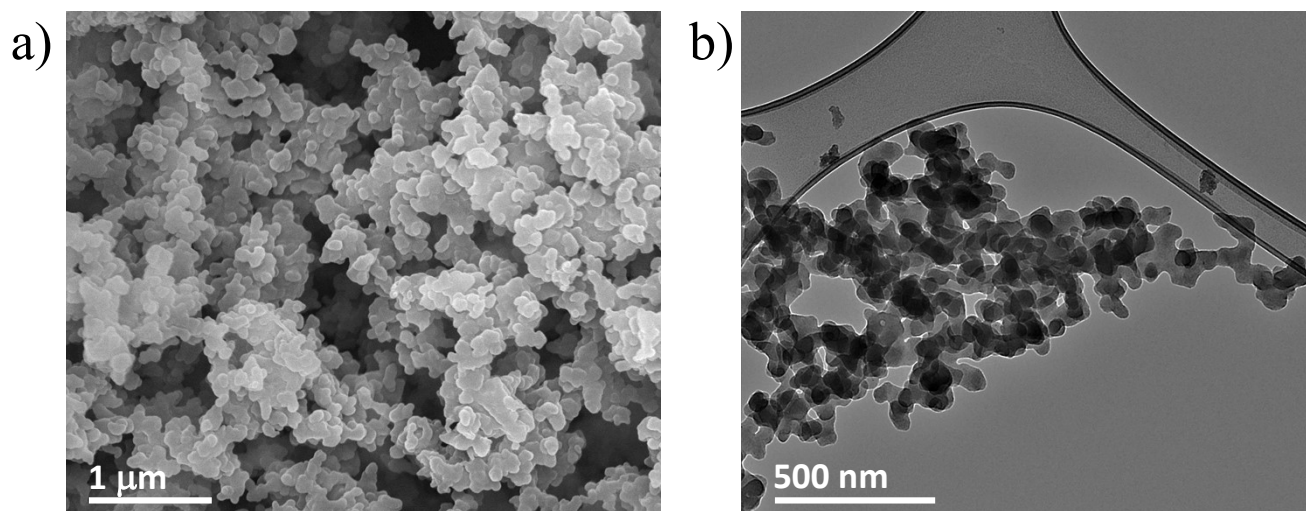
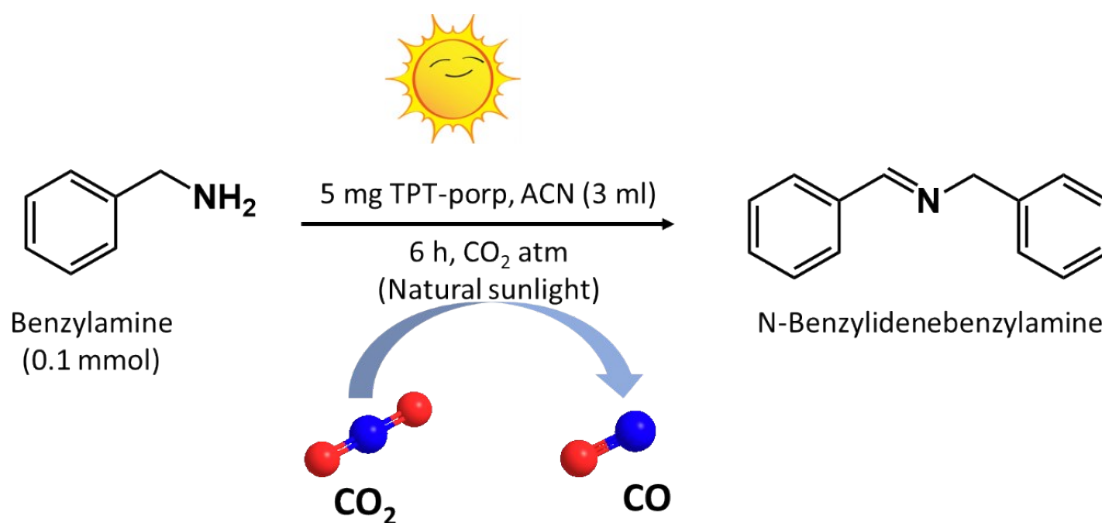
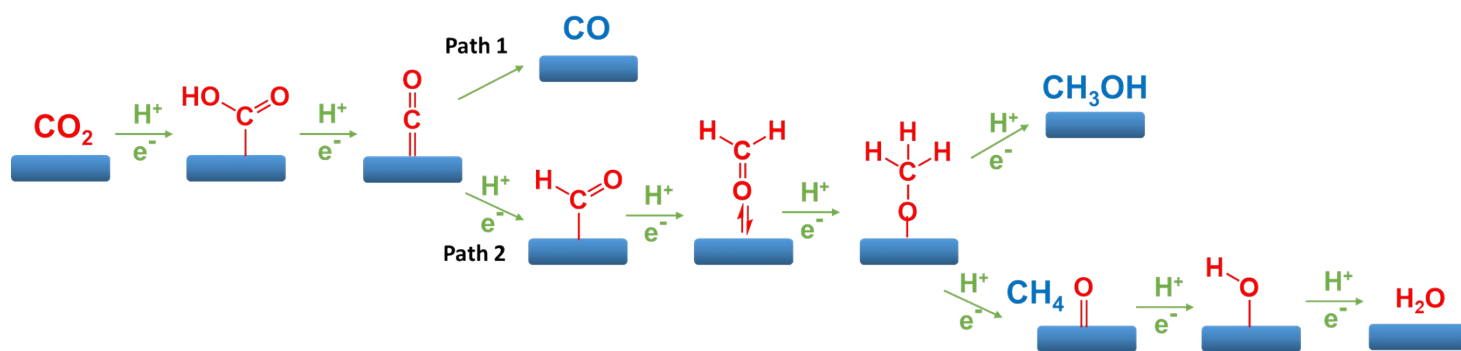


Fig. S26 a) FESEM and b) TEM images of TPT-porp after recyclability.

Supplementary scheme:



Scheme S1 Reaction scheme for photoredox reaction catalysed by TPT-porp under natural sunlight.



Scheme S2 Steps involved in CO_2 reduction pathway.

Supplementary Tables:

Table S1 Previously reported photocatalyst for simultaneous CO₂ reduction and oxidation of organic substrate.

S. No.	Catalyst	Substrate	Light source	Oxidation product (Activity and selectivity)	Reduction product (Activity and selectivity)	AQY/STF (%)	Ref
1	CdS-TiO ₂	Cyclohexanol	250 W high pressure Hg lamp	Cyclohexanone (20 μmolg ⁻¹ h ⁻¹ ; N.A.)	HCOOH (N.A.; N.A.), cyclohexyl formate (20.2 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	3
2	Ag-TiO ₂	Benzyl Alcohol	300 W Xe lamp	Benzaldehyde (N.A.; 98%)	CH ₃ OH (7.47 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	4
3	Py-PCN (loaded with 3 wt% Pt)	Cyclohexene	300 W Xe lamp	Cyclohexanol (75 μmolg ⁻¹ h ⁻¹ ; N.A.)	CO (28 μmolg ⁻¹ h ⁻¹ ; N.A.), HCOOH (55 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	5
4	Keplerate Mo132	Phenylacetylene	Blue LED light	Acetophenone (0.79 mmol; N.A.)	HCOOH (0.12 mmol; N.A.)	N.A.	6
5	Pd/TiO ₂	Ethane	300 W Xe lamp UV light	Ethene (230.5 μmolg ⁻¹ h ⁻¹ ; 95.42%)	CO (120.4 μmolg ⁻¹ h ⁻¹ ; 44%), H ₂ (162.2 μmolg ⁻¹ h ⁻¹ ; 55%)	0.93%	7
6	Cu ₂ O/Cu	Benzyl Alcohol	300 W Xe lamp, λ > 420 nm	Benzylacetate (116.7 μmolg ⁻¹ h ⁻¹ ; N.A.)	CO (0.65 μmolg ⁻¹ h ⁻¹ ; N.A.), H ₂ (1 μmolg ⁻¹ h ⁻¹ ; N.A.), HCOOH (2.5 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	8
7	CdSe/CdS QDs	1-phenylethanol	450 nm LED light	Pinacol (26.5 mmolg ⁻¹ h ⁻¹ ; 96%)	CO (27.63 mmolg ⁻¹ h ⁻¹ ; 94%)	N.A.	9
8	g-CN/POM/[Re]	Cyclohexene	White LED light	1,3 cyclohexadiene (72.5 μmolg ⁻¹ h ⁻¹ ; N.A.), benzene (11.3 μmolg ⁻¹ h ⁻¹ ; N.A.)	CO (127.5 μmolg ⁻¹ h ⁻¹ ; 100%)	N.A.	10
9	CsPbBr ₃ /Cs ₄ PbBr ₆	CH ₃ OH	300 W Xe lamp	HCOOH (56.5 μmolg ⁻¹ h ⁻¹ ; N.A.)	CO (120.16 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	11
10	FAPbBr ₃ /Bi ₂ WO ₆	Benzyl Alcohol	300 W Xe lamp AM 1.5G	Benzaldehyde (250 μmolg ⁻¹ h ⁻¹ ; N.A.)	CO (170 μmolg ⁻¹ h ⁻¹ ; ~100%)	1.2 (λ=400 nm)	12
11	Black phosphorous QDs (BP)-ZnIn ₂ S ₄	Benzylamine	300 W Xe lamp, λ > 420 nm	N-benzylidene-benzylamine (1400 μmolg ⁻¹ h ⁻¹ ; 94%)	CO (750 μmolg ⁻¹ h ⁻¹ ; 35%), H ₂ (1360 μmolg ⁻¹ h ⁻¹ ; 65%)	6.5% (λ=465 nm)	13
12	3DOM CdSQD/NC	Benzylamine	300 W Xe Lamp λ > 420 nm	N-benzylidene-benzylamine (9.82 μmolg ⁻¹ h ⁻¹ ; 95.3%)	CO (5.21 μmolg ⁻¹ h ⁻¹ ; 89.6%)	2.90 (λ=450 nm)	14
13	CN-KRb	Ethanol	5 W white LED (100 mW/cm ²)	CH ₃ CHO (1212.3 μmolg ⁻¹ h ⁻¹ ; 93%)	CH ₃ CHO (1212.3 μmolg ⁻¹ h ⁻¹ ; 93%)	N.A.	15
14	ZnV ₂ O ₆ @WO ₃ -g-C ₃ N ₄	Benzylamine	350 W xenon lamp	N-benzylidene-benzylamine (yield = 55%)	CO (279 μmolg ⁻¹ h ⁻¹ ; N.A.), CH ₄ (113 μmolg ⁻¹ h ⁻¹ ; N.A.)	N.A.	16
15	TPT-porp (metal-free)	Benzylamine	Natural sunlight	N-benzylidene-benzylamine (2123 μmolg⁻¹h⁻¹; 98%)	CO (1786 μmolg⁻¹h⁻¹; 93%)	AQY = 9.34% (λ=430 nm)/ STF = 0.24%	This work

N.A.- Not Applicable

Table S2 Optimization of synthesis of TPT-porp.

S. No.	Solvent	Temp/Time	BET S.A. (m ² /g)	Yield (%)
1.	Mesitylene/ 1,4-Dioxane/ 6 M AcOH (1:2:0.2)	120 °C/ 3 days	44	73
2.	Mesitylene/ 1,4-Dioxane/ 6 M AcOH (1:1:0.2)	120 °C/ 3 days	52	78
3.	o-DCB/ n-Butanol/ 6 M AcOH (1:2:0.2)	120 °C/ 3 days	88	82
4.	o-DCB/ n-Butanol/ 6 M AcOH (1:1:0.2)	120 °C/ 3 days	97	80
5.	o-DCB/ n-Butanol/ 12 M AcOH (1:1:0.2)	120 °C/ 4 days	120	84
6.	o-DCB/n-Butanol/ 12 M AcOH (1:1:0.2)	140 °C/ 4 days	248	85

Reaction conditions: TPT (1 eq), porp-NH₂ (0.75 eq), solvent, sealed under inert atmosphere.

S.A.- surface area

Table S3 Elemental Analysis of TPT-porp under solvent free conditions.

Elements	Experimental value (%)	Theoretical value (%)
C	72.93	75.95
N	16.15	14.76
H	4.38	3.89

Table S4 The sunlight intensities and temperatures during the photocatalytic study.

S. No.	Date	Temperature (°C)							Average temperature (°C)	Average Sunlight intensity (mW/cm ²)
		Temperature at each hour (°C)								
1	24/06/2022	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	35.4	52.19
		33	34	35	36	37	37	36		
2	28/06/2022	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	38.4	44.65
		36	37	38	39	40	40	39		
3	04/07/2022	10:30 AM	11:30 AM	12:30 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	33.3	22.38
		34	35	35	34	32	32	31		
4	16/07/2022	10:00 AM	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	33.1	40.35
		31	34	35	36	34	32	30		
5	24/07/2022	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	31.7	37.74
		31	33	32	31	32	32	31		
6	02/08/2022	10:30 AM	11:30 AM	12:30 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	33.0	32.56
		31	32	33	34	35	34	32		
7	09/08/2022	10:00 AM	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	34.3	57.64
		32	33	33	34	36	37	35		
8	18/08/2022	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	33.8	55.47
		32	33	34	35	35	34	34		

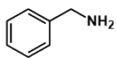
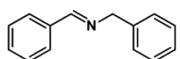
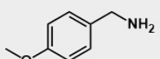
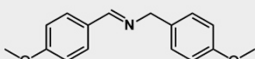
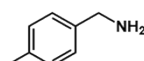
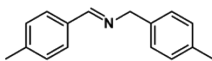
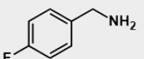
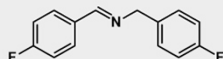
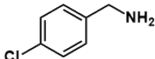
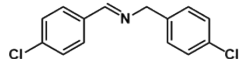
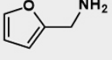
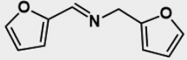
9	26/08/2022	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	06:00 PM	33.7	50.98
		33	34	34	35	35	34	34		
10	05/09/2022	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	05:00 PM	33.3	26.82
		33	34	34	35	34	33	33		
11	21/09/2022	10:00 AM	11:00 AM	12:00 PM	01:00 PM	02:00 PM	03:00 PM	04:00 PM	31.8	39.27
		30	31	32	32	33	33	32		

Table S5 Wavelength dependent Apparent Quantum Yield (AQY%) for CO.

S. No.	Wavelength λ (nm)	Intensity I (Wcm^{-2})	Amount of CO η_{CO} (mol)	AQY (%)
1.	400	0.00084	4.08×10^{-6}	6.27
2.	430	0.00046	3.57×10^{-6}	9.34
3.	450	0.00117	4.35×10^{-6}	4.26
4.	500	0.00166	5.11×10^{-6}	3.17
5.	550	0.00210	7.88×10^{-6}	3.52
6.	600	0.00200	3.09×10^{-6}	1.33

Conditions: TPT-porp (5 mg), light source- 400 W Xenon lamp using band pass filters of different wavelength, Irradiation time ($t = 2$ h), Area of irradiation ($A = 6.44 \text{ cm}^2$)

Table S6 Substrate scope of simultaneous CO₂ reduction and oxidative amine homocoupling.

S. No.	Substrate	Product	Oxidation product	Reduction Product		e ⁻ /h ⁺ ratio ^c
				Imine ^a ($\mu\text{molg}^{-1}\text{h}^{-1}$)	CO ^b ($\mu\text{molg}^{-1}\text{h}^{-1}$)	
1			2123	1786	114	1.08
2			2360	2498	53	1.14
3			1422	1370	80	1.17
4			1815	1934	73	1.22
5			1184	1665	79	0.97
6			1190	1249	43	1.19

Reaction Conditions: Amine (0.1 mmol), photocatalyst TPT-porp (5 mg), ACN (3 ml), time 6 h, and natural sunlight.

^adetermined by GCMS

^bdetermined by GC

^cThe ratio of consumption of electrons to holes in redox process is calculated using the formula $n(e^-)/n(h^+)$
 $n(e^-) = 2 \cdot n(\text{CO}) + 8 \cdot n(\text{CH}_4)$ and $n(h^+) = 2 \cdot n(\text{imine})$

where $n(\text{CO})$, $n(\text{CH}_4)$ and $n(\text{imine})$ are the rate of formation of CO, CH₄ and imine respectively (in $\mu\text{molg}^{-1}\text{h}^{-1}$)

Table S7 Total energy (eV) directly obtained from DFT of the pristine TPT-porp, corresponding intermediates and species.

Species	Gibbs free energies, ΔG (eV)
Catalyst (*)	-3596.559763
CO ₂	-188.597975
CO ₂ *	-3785.150649
COOH*	-3785.688547
CO*	-3709.875894
CHO*	-3710.411678
CO	-113.325129

Table S8 Gibbs free energy (ΔG) in eV for adsorption of CO₂ at porphyrin and imine

Active site	Gibbs free energy (Eh)	Rel. Gibbs free energy diff. (kJ/mol)
Imine	-3785.147619	7.95
Porphyrin	-3785.150649	0

Table S9 Relative Gibbs free energy (ΔG) in eV of CO₂ photoreduction for the TPT-porp and corresponding intermediates.

Catalyst	$\Delta G_{[\text{COOH}^*]}$	$\Delta G_{[\text{CO}^*]}$	$\Delta G_{[\text{CO}]}$	$\Delta G_{[\text{CHO}^*]}$
TPT-porp	1.52	0.9	0.657	2.28

References

- 1 D. C. Tahmassebi, T. Sasaki, *J. Org. Chem.* 1994, **59**, 679–681.
- 2 M. Dinari, M. Hatami, *J. Environ. Chem. Eng.* 2019, **7**, 102907.
- 3 G. Song, F. Xin, J. Chen, X. Yin, *App. Catal. A: Gen.* 2014, **473**, 90–95.
- 4 L. Wang, X. Zhang, L. Yang, C. Wang, H. Wang, *Catal. Sci. Technol.* 2015, **5**, 4800–4805.
- 5 X. Gong, S. Yu, M. Guan, X. Zhu, C. Xue, *J. Mater. Chem. A* **2019**, **7**, 7373–7379.
- 6 J. Lodh, A. Mallick, S. Roy, *J. Mater. Chem. A* 2018, **6**, 20844–20851.
- 7 R. Zhang, H. Wang, S. Tang, C. Liu, F. Dong, H. Yue, B. Liang, *ACS Catal.* 2018, **8**, 9280–9286.
- 8 Y. Chen, M. Wang, Y. Ma, Y. Li, J. Cai, Z. Li, *Catal. Sci. Technol.* **2018**, **8**, 2218–2223.
- 9 Q. Guo, F. Liang, X.-B. Li, Y.-J. Gao, M.-Y. Huang, Y. Wang, S.-G. Xia, X.-Y. Gao, Q.-C. Gan, Z.-S. Lin, C.-H. Tung, L.-Z. Wu, *Chem* 2019, **5**, 2605–2616.
- 10 H. Yu, E. Haviv, R. Neumann, *Angew. Chem. Int. Ed.* 2020, **132**, 6278–6282.
- 11 G.-X. Dong, W. Zhang, Y.-F. Mu, K. Su, M. Zhang, T.-B. Lu, *Chem. Commun.* 2020, **56**, 4664–4667.
- 12 H. Huang, J. Zhao, Y. Du, C. Zhou, M. Zhang, Z. Wang, Y. Weng, J. Long, J. Hofkens, J. A. Steele, M. B. J. Roeffaers, *ACS Nano* 2020, **14**, 16689–16697.
- 13 C. Han, Y. Li, J. Li, M. Qi, Z. Tang, Y. Xu, *Angew. Chem. Int. Ed.* 2021, **133**, 8041–8049.
- 14 F. Wang, T. Hou, X. Zhao, W. Yao, R. Fang, K. Shen, Y. Li, *Adv. Mater.* 2021, **33**, 2102690.
- 15 Q. Liu, J. Lin, H. Cheng, L. Wei, F. Wang, *Angew. Chem. Int. Ed.* 2023, **62**, e202218720.
- 16 P. K. Prajapati, N. Saini, D. K. Chauhan, K. Kailasam, *J. Mater. Chem. A* 2022, **11**, 385–400.