

## Supporting Information

### **Constructing Metal-Free 2D Covalent Organic Framework for Visible-Light-Driven Photocatalytic Reduction of CO<sub>2</sub>: a Sustainable Strategy for Atmospheric CO<sub>2</sub> Utilization**

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## **Instrumentation**

**Absorption spectroscopy:** UV-Vis absorption spectra of the catalyst was recorded on SHIMADZU, UV-2600 UV-Vis spectrometer with a standard 1 cm x 1 cm cuvette.

**NMR Spectra:** <sup>1</sup>H NMR (Proton nuclear magnetic resonance spectra) were performed on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm).

**PXRD:** The PXRD analysis of the photocatalyst (BTD-TTA COF) was executed by using an X-ray diffractometer (BRUKER, Powder X-Ray ecoD8 ADVANCE) equipped with Ni-filtered Cu K $\alpha$  ( $\lambda$  = 0.15406 nm) radiation.

**IR Spectra:** The FTIR spectra of the synthesized and starting materials were conducted by using a Perkin-Elmer spectrophotometer (FT-IR 783) on KBr Pellets.

**FESEM:** FESEM images of the catalyst were acquired by using Scanning Electron Microscope (SEM) [JEOL JSM IT 300], which help to know about the morphological information of the sample.

**TEM:** Transmission Electron Microscope (TEM) [JEOL JEM 2100] was used to get the morphological information of the sample.

**TGA:** The thermal stability of the COF material was analyzed by a Thermogravimetric Analyzer [Model: Perkin Elmer-Pyris-Diamond, TG/DTA] at the rate of 10 °C per min up to 800 °C in presence of air.

**BET:** The N<sub>2</sub> adsorption-desorption analysis of BTD-TTA COF sample was conducted by using a BET Surface Analyzer [QUANTACHROME ASIQC602-5].

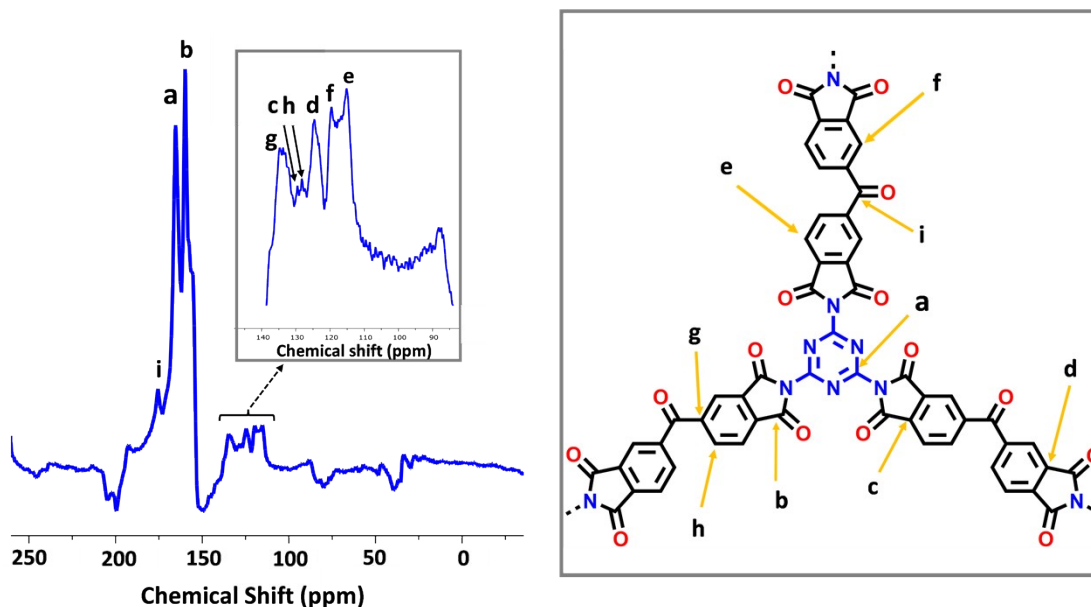
**Fluorescence Spectroscopy:** The Fluorescence Emission spectra was recorded by using Horiba Fluoro Max 4 spectrometer.

**CHN Analysis:** A CHNOS elemental analyzer (Vario EL III) was performed to find out the contents of C, N and H in BTD-TTA COF.

**EIS analysis:** The measurements have been performed in 0.1 M PBS solution and a conventional three-electrode system where BTD-TTA COF on the glassy carbon electrode is used as the working electrode and double junction Ag/AgCl saturated with 3.0M KCl is used as a reference electrode. The Platinum wire served as a counter electrode. The electrochemical impedance spectroscopy (EIS) has been carried out in the frequency range of 100 kHz -0.01 Hz with an AC amplitude of 10 mV at a constant the applied potential of 5 mV.

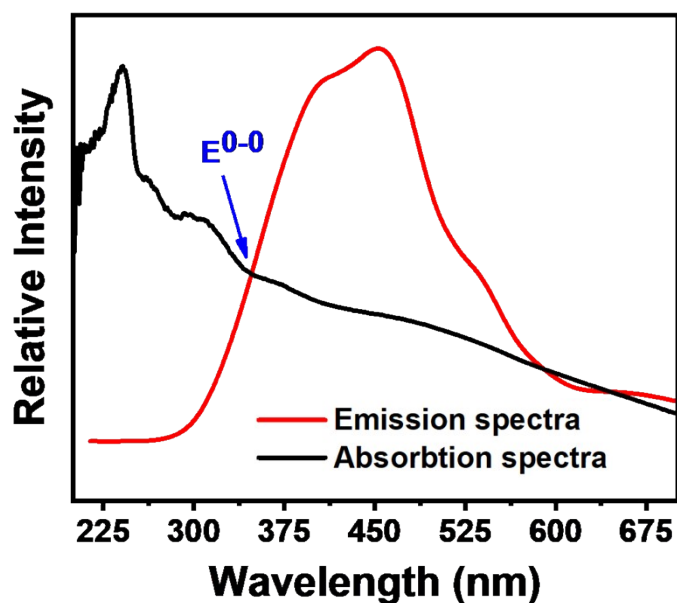
### Chemicals :

Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (M= 322.23 g/mol) (BTD) and Tributyl amine (TBA) were obtained from Sigma Aldrich, India. Dimethyl acetamide was procured from TCI, India. 1,3,5-triazine-2,4,6-triamine (M= 126.12g/mol), acetone, ethanol, hexanes, tetrahydrofuran (THF), N, N-dimethylformamide and m-cresol, Dimethyl sulfoxide (DMSO) were brought from Merck, India and used without further purification. Triethyl amine and triethanolamine were also purchased from Merck, India and used as received.

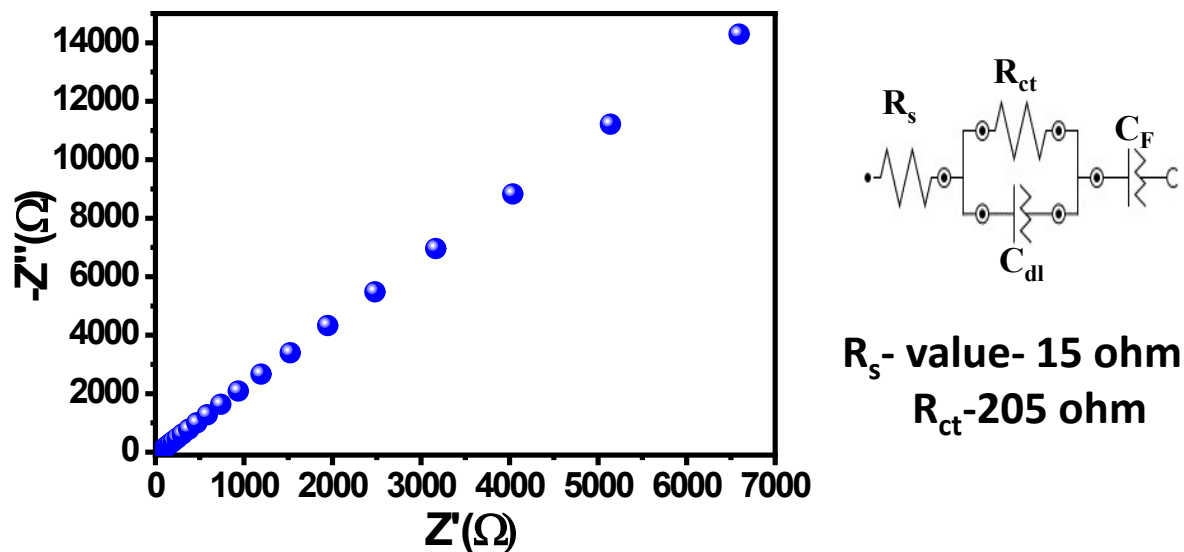


**Figure S1.**  $^{13}\text{C}$  solid state NMR of the model compound (i.e., the 2D COF photocatalyst, BTD-TTA COF).

As described in Fig. S1, solid-state  $^{13}\text{C}$  NMR spectroscopy detects the C signal at 159.7 ppm from the carbonyl carbon of the imide ring and the carbon signal for the triazine unit at 165.3 ppm for the imide-bound COF network. These data suggest that the synthesized COF material ensures the formation of 2 D COF structure. A comparative diagram is shown here for better understanding (Fig. S1).

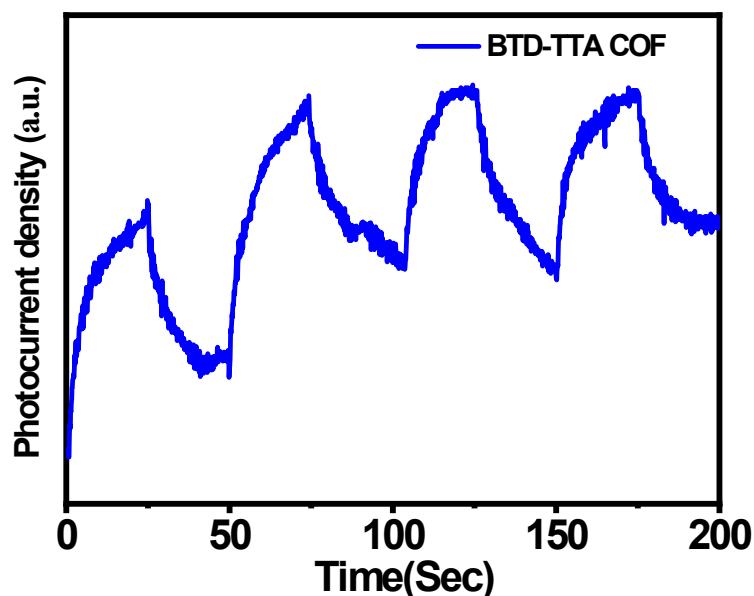


**Figure S2.** Normalized absorption (black line) and emission spectra (red line) of BTD-TTA COF.



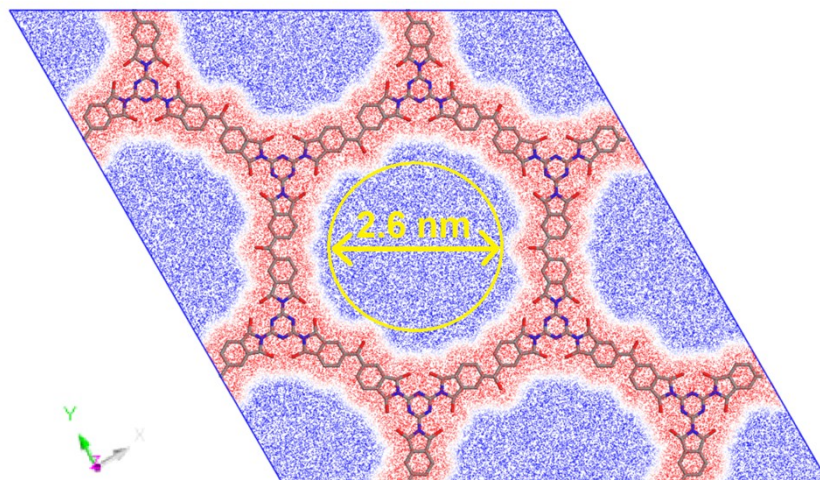
**Figure S3.** The EIS Nyquist plot of BTD-TTA COF.

For a clear understanding about the charge transfer behavior of the synthesized catalyst, electrochemical impedance spectroscopy (EIS) of BTD-TTA COF was executed in 0.1 M PBS solution and relative Nyquist plot was studied which indicating that the COF possesses good interface layer and charge transfer resistances. The straight line of EIS spectroscopy signifies a better electronic conductivity under light irradiation. The series resistance ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ) values are found to be 15 ohm and 205 ohm respectively.

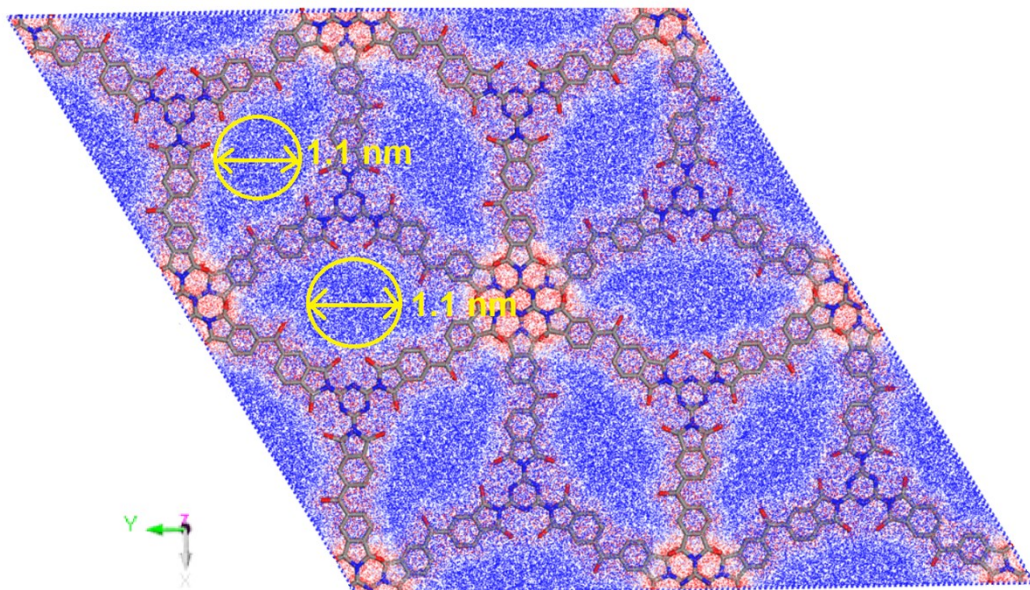


**Figure S4.** The transient photocurrent responses of BTD-TTA COF upon light illumination.

The significantly strong and fast transient photocurrent response of COF material under visible-light irradiation suggests that a higher separation efficiency of the photogenerated electron-hole pairs was attained inside the COF framework [1]. So, all of these results (EIS Nyquist and photocurrent responses) indicate that the COF has enhanced visible-light absorption capacity which promoted the separation of photogenerated electron-hole pairs and as a result photocatalytic activity of the synthesized COF increases.



**Figure S5.** The AA stacking model of BTD-TTA COF based on Connolly surface function, showing a pore channel diameter of about 2.6 nm.



**Figure S6.** The AB stacking model of BTDA-TTA COF based on Connolly surface function, showing a pore channel diameter of about 1.1 nm.

**AA-eclipsed stacking model**

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**Table S1.** Atomic coordinates of the AA-stacking mode of BTDA-TTA COF

AA-eclipsed stacking model							
Site		Sym.	x	y	z	Occ.	U
1	C	C2	0.04321	0.49928	0.00512	1.000	1.000
2	C	C4	0.09520	0.51034	0.02455	1.000	1.000
3	C	C7	0.34010	0.59425	0.15882	1.000	1.000
4	C	C8	0.36539	0.56843	0.15908	1.000	1.000
5	O	O1	0.11009	0.48141	0.06343	1.000	1.000
6	H	H2	0.30458	0.57806	0.28542	1.000	1.000
7	H	H3	0.34956	0.53304	0.28824	1.000	1.000
8	C	C1	-0.00000	0.54628	0.00000	1.000	1.000
9	H	H1	-0.00000	0.58103	-0.00000	1.000	1.000
10	C	C6	0.28096	0.64048	-0.00000	1.000	1.000
11	N	N1	0.12482	0.56241	-0.00000	1.000	1.000
12	C	C9	0.41147	0.58853	-0.00000	1.000	1.000
13	N	N7	0.33333	0.66667	0.00000	1.000	1.000

AB-staggered stacking model

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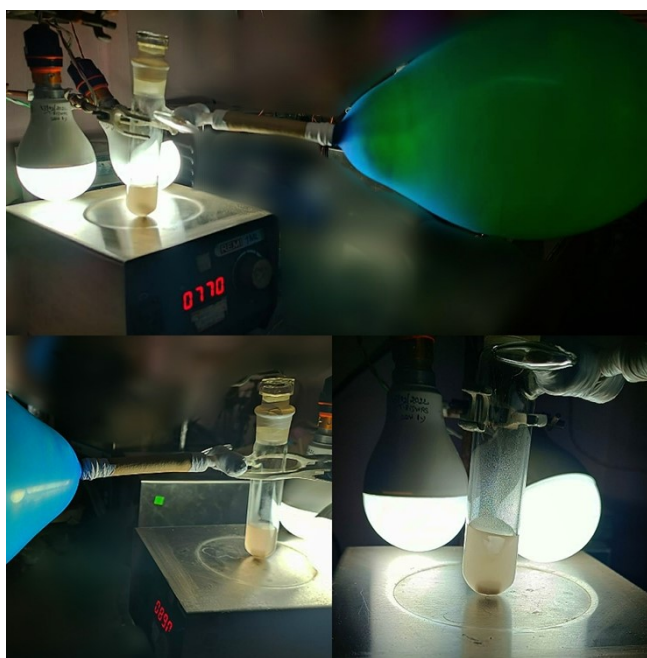
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**Table S2.** Atomic coordinates of the AB-stacking mode of BTd-TTA COF.

AB-staggered stacking model							
			x	y	z	Occ.	U
1	C	C1	-0.33333	-0.12013	0.24998	1.000	1.000
2	C	C2	-0.29010	-0.16745	0.25081	1.000	1.000
3	C	C4	-0.23799	-0.15649	0.25401	1.000	1.000
4	C	C7	0.00651	-0.07227	0.32301	1.000	1.000
5	C	C8	0.03224	-0.09778	0.32445	1.000	1.000
6	C	C35	0.62334	-0.16594	0.25080	1.000	1.000
7	C	C37	0.57117	-0.17692	0.25452	1.000	1.000
8	C	C40	0.32546	-0.26260	0.33208	1.000	1.000
9	C	C41	0.30005	-0.23672	0.33135	1.000	1.000
10	O	O1	-0.22289	-0.18561	0.26075	1.000	1.000
11	O	O7	0.55605	-0.14789	0.26233	1.000	1.000
12	H	H1	-0.33333	-0.08513	0.24988	1.000	1.000
13	H	H2	-0.02918	-0.08805	0.38062	1.000	1.000
14	H	H3	0.01680	-0.13315	0.38270	1.000	1.000
15	H	H17	0.36006	-0.24818	0.39599	1.000	1.000
16	H	H18	0.31485	-0.20201	0.39355	1.000	1.000
17	C	C6	-0.05227	-0.02614	0.25000	1.000	1.000

18	N	N1	-0.20833	-0.10416	0.25000	1.000	1.000
19	C	C9	0.07800	-0.07800	0.25000	1.000	1.000
20	C	C42	0.25545	-0.25545	0.25000	1.000	1.000
21	C	C39	0.38560	-0.30720	0.25000	1.000	1.000
22	N	N4	0.54155	-0.22923	0.25000	1.000	1.000
23	N	N7	0.00000	-0.00000	0.25000	1.000	1.000
24	N	N8	0.33333	-0.33333	0.25000	1.000	1.000

### Reaction set-up:



**Figure S7.** Images of the photoreaction setup with CO<sub>2</sub> balloon directly irradiated with the white LEDlight.

### Photocatalytic Experiment:

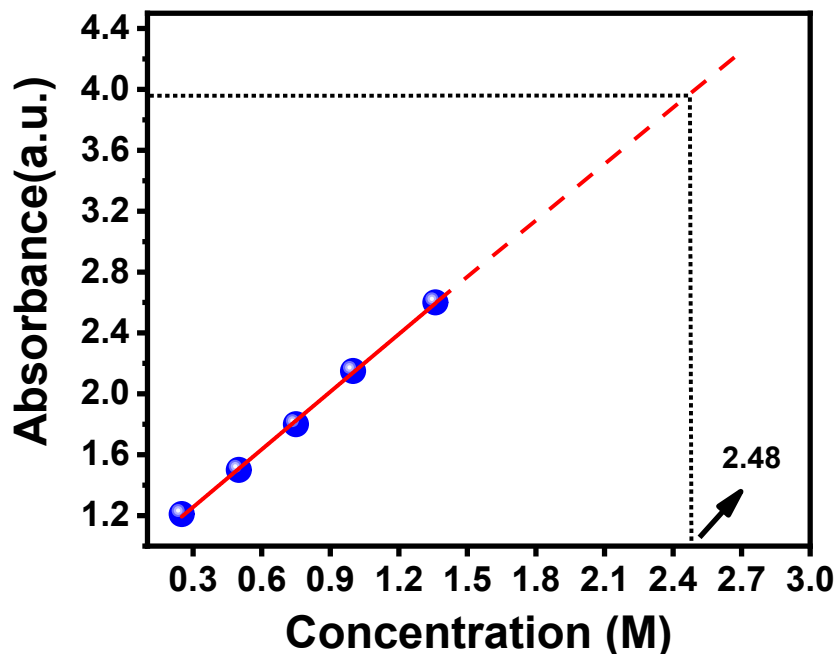
In a general process of photocatalytic carbon dioxide reduction, 10 mg 2D covalent organic framework (BTD-TTA COF) as photocatalyst and tributyl amine (2 mmol) as sacrificial electron donor were added in CH<sub>3</sub>CN (5 mL) in a 50 mL capacity container. At first, the reaction mixture was degassed to remove the dissolved air and then purged with CO<sub>2</sub> for 30 min. After that, the

vessel was closed tightly with a septum with constant stirring under CO<sub>2</sub> atmosphere under of whitelightirradiation by using40 W light-emitting diode (LED). After completion of the reaction, the photocatalyst was separated by centrifugation and the obtained liquid products were confirmed by UV-vis spectrophotometer and GC-FID. The separated photocatalyst was recycled and used for further experiments.

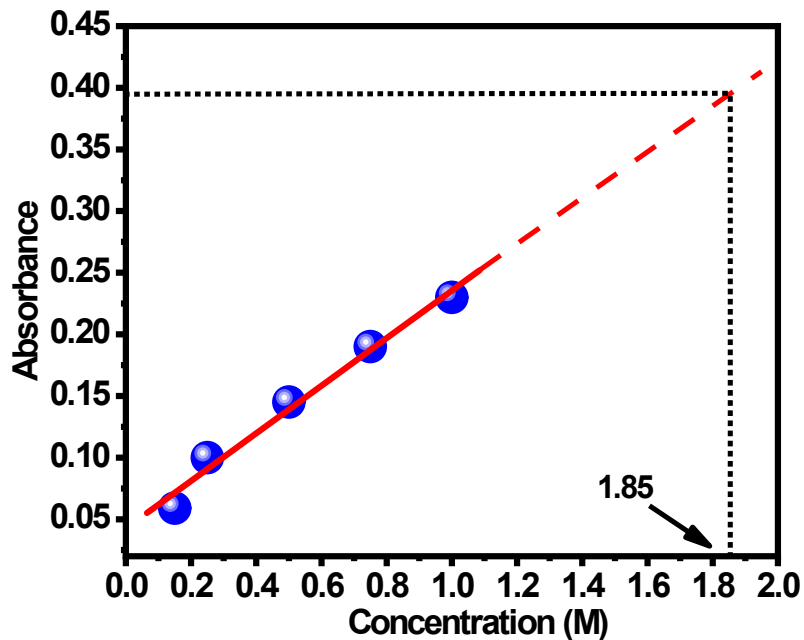
#### Calculation of productionrate of products:

Production ratesof HCOOH and HCHO were calculated using calibration plot as shown in Figures S4 and S5, in which known concentration of HCOOH and HCHO were plotted with the O.D. value in UV-visspectra to obtain the concentrations of produced HCOOH and HCHO.

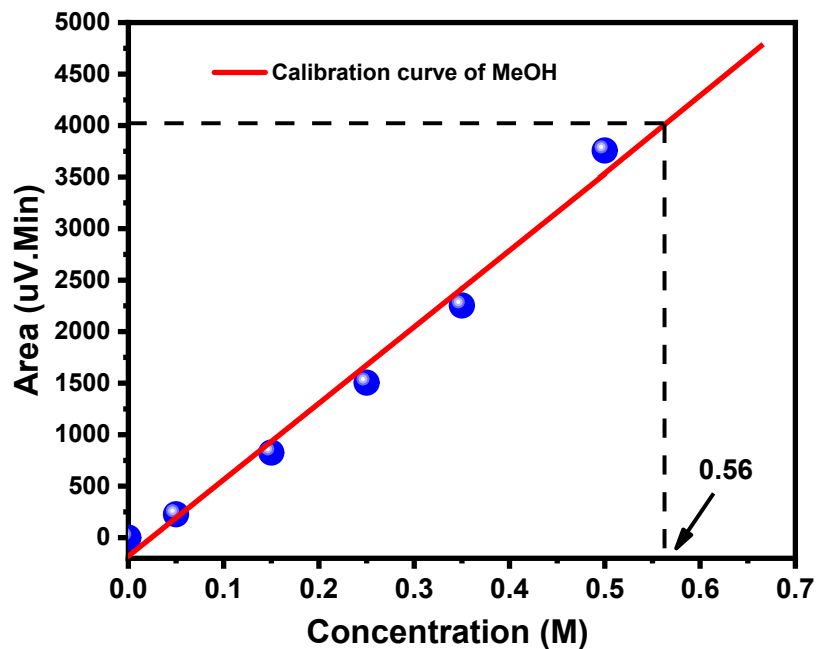
To determine the rate of production of methanol, known concentration of methanol was plotted against the area ( $\mu\text{v. min}$ ) of the peak obtained from GC-FID (Figure S6).



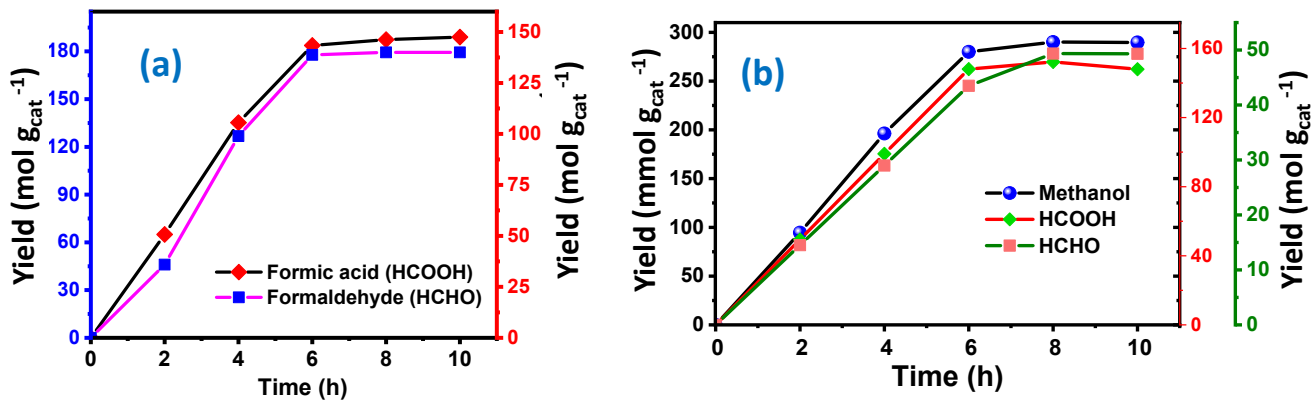
**Figure S8.** Calibration curve of formic acid (HCOOH) for determination of concentration of HCOOH produced.



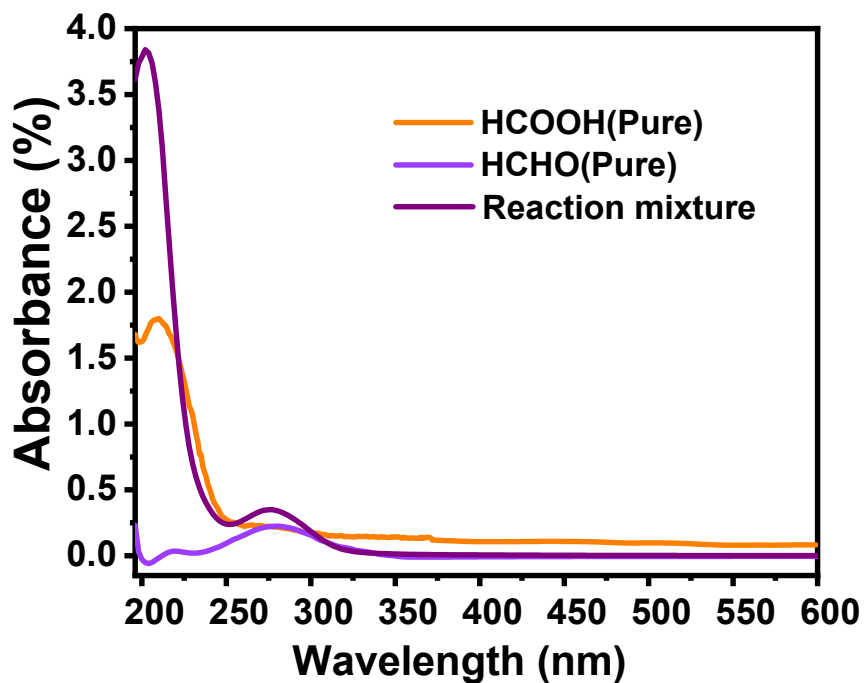
**Figure S9.** Calibration curve of formaldehyde (HCHO) for determination of concentration of produced formaldehyde.



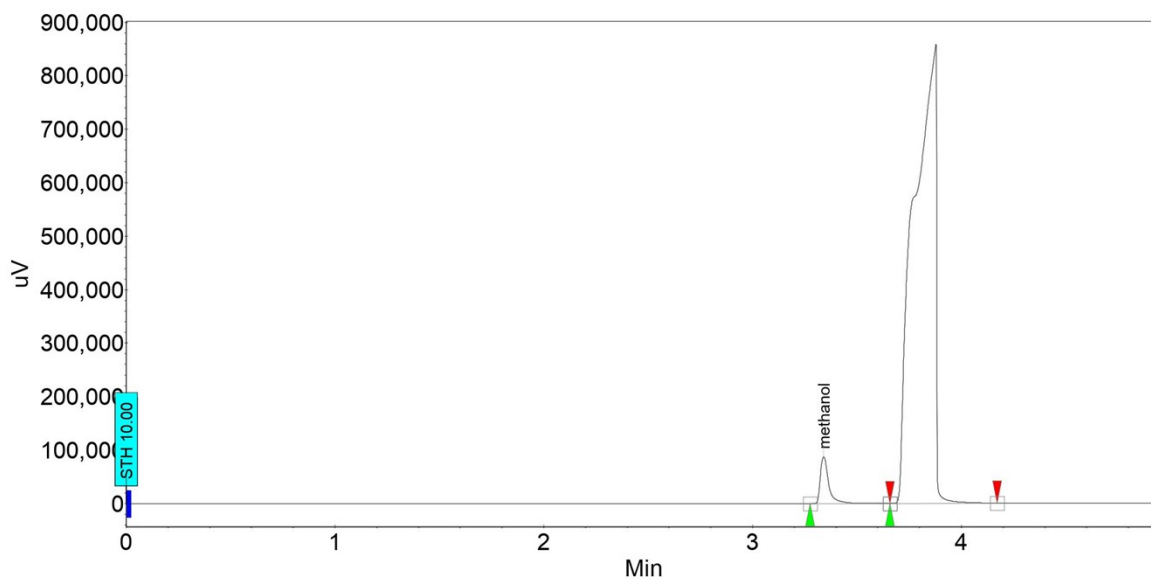
**Figure S10.** Calibration curve (Area vs Concentration) based on GC-FID of methanol (CH<sub>3</sub>OH) for determination of concentration of produced methanol.



**Fig. S11:** Rate of production of (a) HCOOH and HCHO in H<sub>2</sub>O & (b) MeOH, HCOOH and HCHO in CH<sub>3</sub>CN over the prepared Photocatalyst under white LED light irradiation.



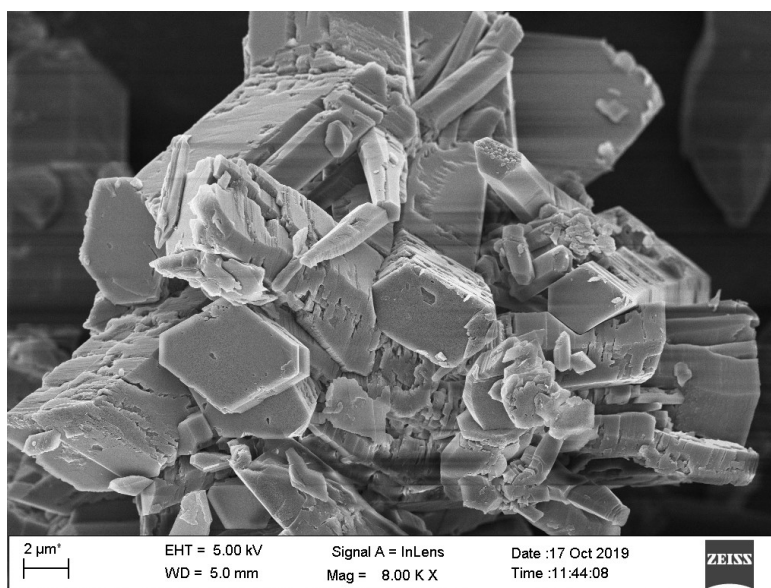
**Figure S12.** Absorption spectra of Pure HCOOH, HCHO and reaction mixture containing HCOOH and HCHO after photocatalytic CO<sub>2</sub> reduction in H<sub>2</sub>O.



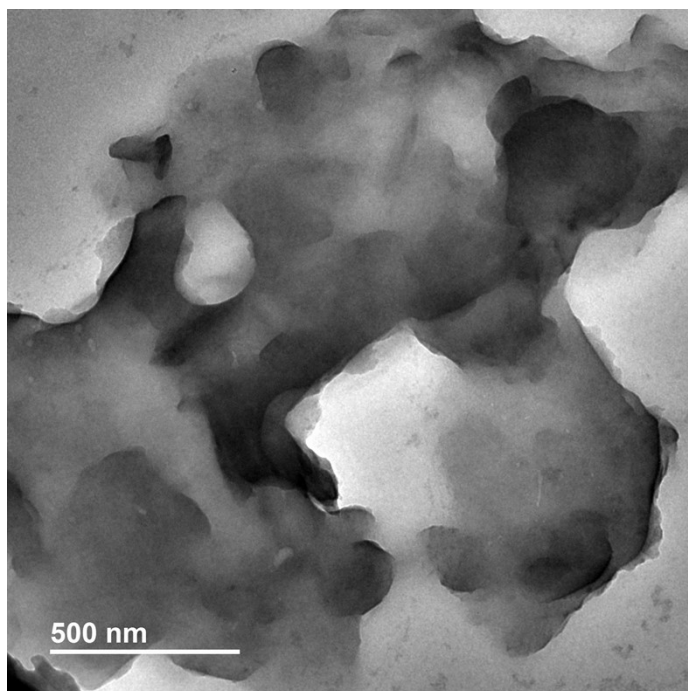
**Peak results :**

Index	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]	Area [uV.Sec]
1	methanol	3.34	87052.8	4017.6	3.712	241053.3
2	UNKNOWN	3.88	858244.1	104220.6	96.288	6253233.8
Total			945297.0	108238.1	100.000	6494287.1

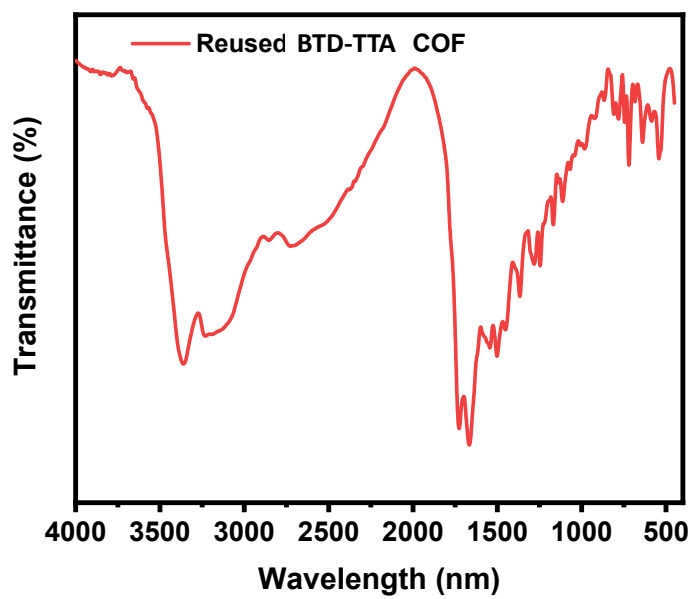
**Figure S13.** GC-FID peak of Methanol after reduction of CO<sub>2</sub> over photocatalyst BTd-TTA under the optimized reaction condition.



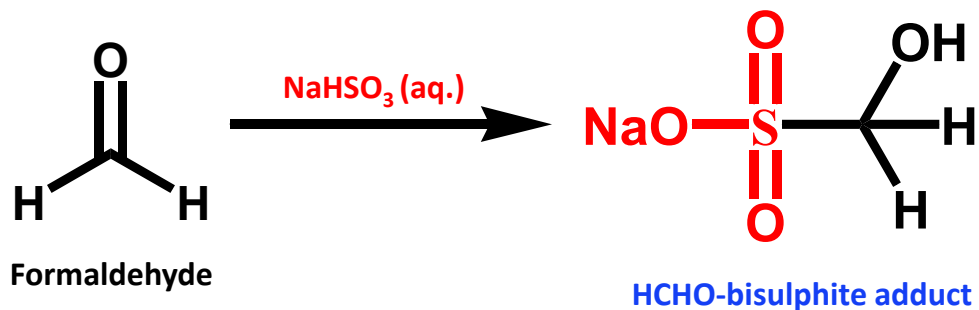
**Figure S14.** FESEM image of reused photocatalyst (BTd-TTA COF).



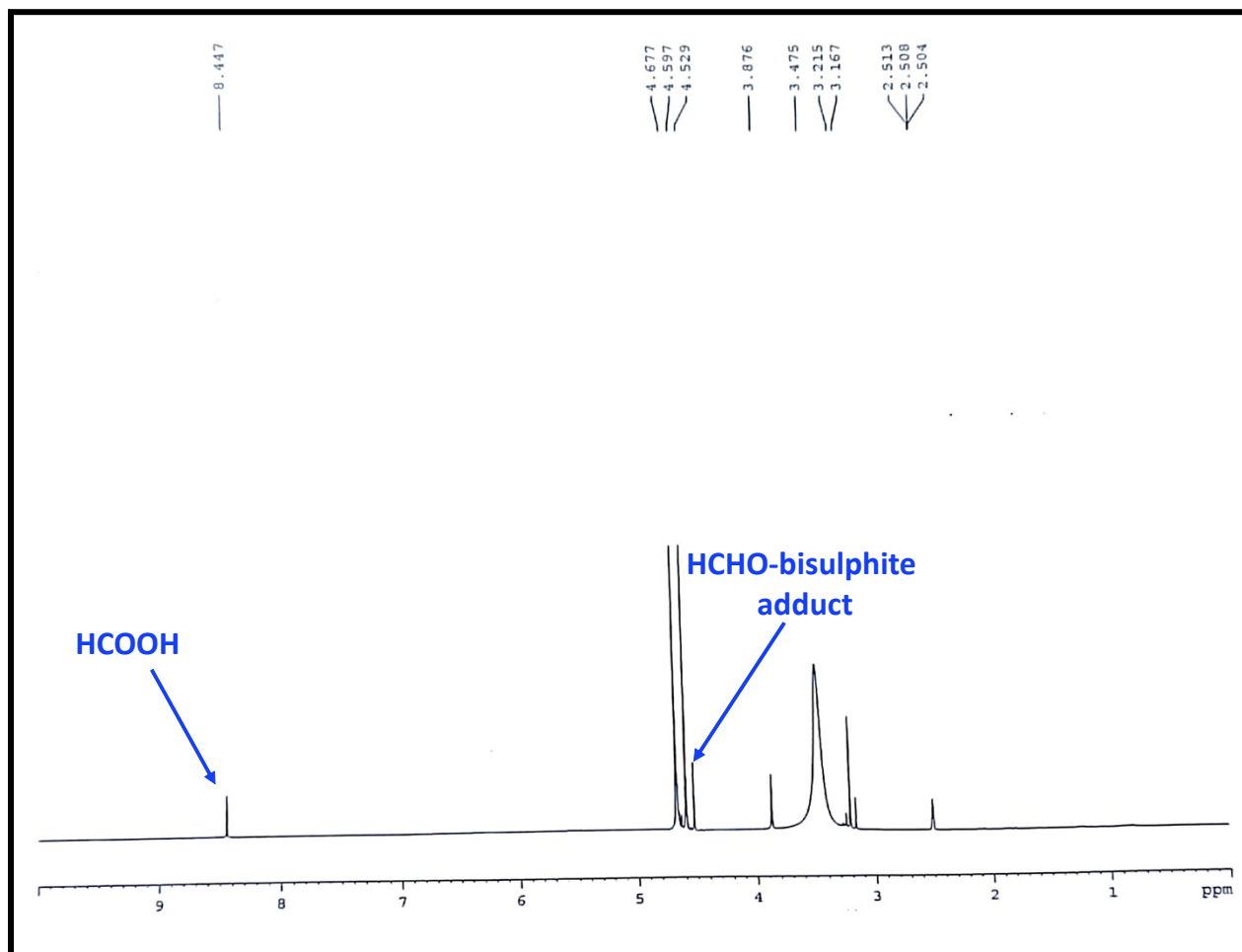
**Figure S15.** TEM image of reused photocatalyst (BTD-TTA COF).



**Figure S16.** IR spectra of recycled BTD-TTA COF catalyst.

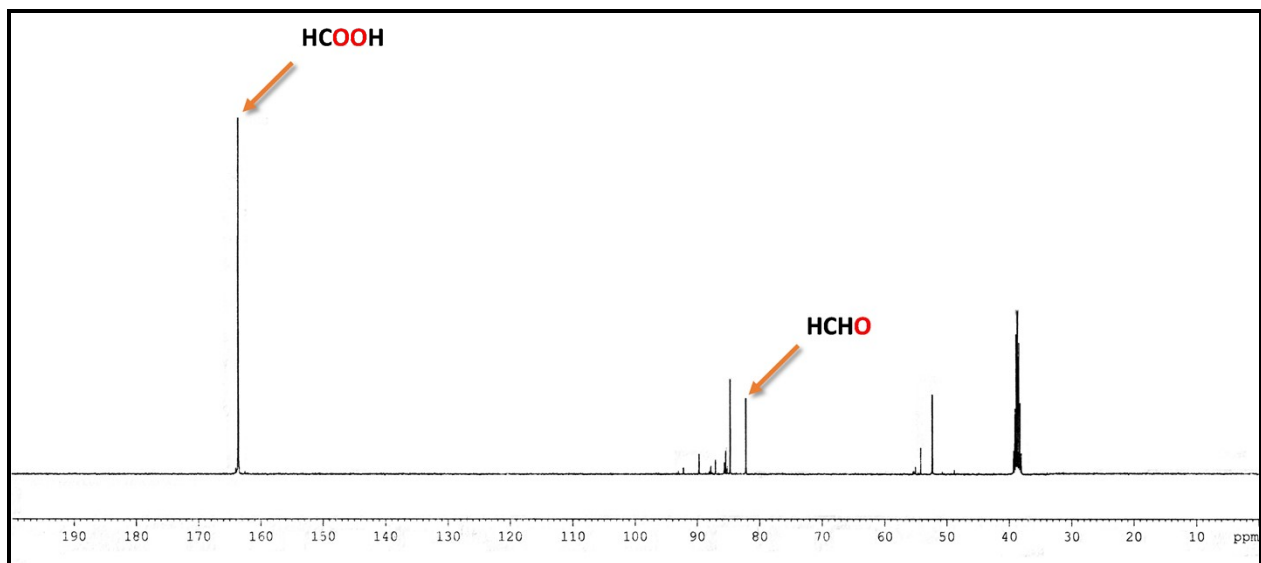


**Scheme S1.** Formation of HCHO-bisulphite adduct from HCHO.



**Figure S17.** <sup>1</sup>H-NMR spectrum of the reaction mixture in DMSO-D<sub>6</sub> after photocatalytic reaction followed by centrifugation and treatment with sodium bisulphite.





**Figure S18.**  $^{13}\text{C}$  NMR spectra of the reaction mixture after photocatalytic reaction.

#### Reference

1. Y.Xie, Y.Zhuo, S.Liu, Y.Lin, D.Zuo, X.Wu, C.Li, P. K. Wong, *Sol. RRL*, 2020, *4*, 1900440.