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Electronic Supplementary Information

Interfacially Synthesized 2D COF Thin Film Photocatalyst: Efficient Photocatalyst for Solar Formic Acid Production from CO₂ and Fine Chemical Synthesis

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Experimental Procedures

1. General remarks

4-Nitrobenzaldehyde, vinyltrifluoroborate, 2-bromo-1,4-dimethylbenzene, pyrrol and Pd(PPh₃)₄ were purchased from Sigma Aldrich. Propionic acid, Glycoxal (30% Aqueous) were procured form TCI, Korea. All α -bromoacetophenones were purchased from Sigma Aldrich. The enzymes and β -nicotinamide adenine dinucleotide were purchased from Sigma Aldrich. All the solvents used in the experiment were of HPLC grade and used without further purification. Ultra-pure water was obtained using a Millipore System (Tech Sinhan Science). The organometallic mediator (Rh), [Cp*Rh(bpy)Cl]Cl, (Cp* = 5-C₅Me₅, bpy = 2,2-bipyridyl) was synthesized as described previously in literature.¹

2. Instruments and Measurements

1H NMR spectra were recorded on a Bruker AVANCE II+ 500 MHz spectrometer with tetramethylsilane (TMS; $\delta = 0$) as internal standard. UV-Visible spectra were recorded on Shimadzu UV-1800 spectrophotometer. The fluorescence decay studies were carried out on Photon Technology TM-200 lifetime spectrofluorometer under excitation of 505 nm. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bruker ALPHA-T FT-IR spectrometer. The test specimens were prepared by the KBr-disk method. XPS spectra were recorded on KRATOS Axis Nova photoelectron spectrometer. A commercial atomic force microscope (Nanoscope; Digital Instruments, Veeco Metrology group), equipped with a J scanner was used to examine morphology of the sample in the tapping mode. SEM analysis was carried out on JEOL-JSM 6700F instrument. High-resolution transmission electron microscope (HRTEM) images were obtained on a FET Phillips instrument [(Model No. 200k VLAB6, (FEL TECNAI G2-20S-Twin)] operating at 200 kV. The formic acid estimation was carried out with ion chromatograph The Metrohm Eco IC System, (Metrohm AG Herisau, Switzerland) equipped with conductometric detector (measuring range 0-15000 μ S/cm) and a MSM II Metrosep A Supp 5 (150 mm × 4 mm, Metrohm AG Herisau, Switzerland). The suppressor and ultraviolet photoelectron spectroscopy (UPS) spectra was measured using AXIS Supra+ instrument with a monochromatic He I light source (21.22 eV).

3. Synthetic Procedure:

3.1. Synthesis of 2-Bromobenzene-1,4-Dicarbaldehyde:²

Sulfuric acid (24 mL) was added dropwise to a mixture of 2-bromo-1,4-dimethylbenzene (5 g), acetic acid (40 mL), and acetic anhydride (65 mL) at 0°C. CrO₃ (17.6 g) was added to the reaction mixture in small portions at 0°C with vigorous stirring. The reaction mixture was further stirred at this temperature for another 12 h until the reaction was completed. The greenish slurry was slowly poured into ice water (500 mL). The product was then extracted with chloroform and the organic layer was washed with NaCl (aq.) and water and dried over anhydrous Na₂SO₄, and concentrated. The solid was then hydrolyzed by refluxing with a mixture of water (40 mL), ethyl alcohol (40 mL), and sulfuric acid (3.5 mL) for 12 h. After the mixture was cooled, it was poured into water (500 mL) and extracted with chloroform. The crude product was purified by chromatography using ethyl acetate and n-hexane (1:4 v/v). White solid was obtained after removal of the solvent (2.1 g). ¹H NMR (500 MHz, CDCl₃, ppm) δ : 10.43(s, 1H; CHO), 10.06(s, 1H; CHO), 8.16(d, 1H, benzo H), 8.07(d, 1H, benzo H), 7.92(dd, 1H, benzo H). ¹³C NMR (125 MHz, CDCl₃, ppm):191.09, 189.97, 140.64, 137.01, 130.51, 128.56, 127.34.

3.2. Synthesis of 2-vinylbenzene-1,4-Dicarbaldehyde:³

1 (2.91g, 13.7 mmol), potassium vinyltrifluoroborate (4.57g, 33.1mmol), K₂CO₃ (11.3g, 82.2mmol), and Pd(PPh₃)₄ (0.456g, 0.411mmol) were dissolved in a mixture of toluene (50mL), THF (50mL) and H₂O (10mL), the resulting mixture was refluxed at 90 °C under N₂ atmosphere for 24h. The residue was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure, giving the crude compound which was purified by flash chromatography with hexane/ethyl acetate (5:1) as eluent to afford the title compound as yellow solid. Yield: 2.23g (87%). ¹H NMR (500 MHz, CDCl₃) δ : 10.37 (s, 1H; CHO), 10.11(s, 1H; CHO), 8.05(s, 1H), 7.98 (d, 2H), 7.91 (dd, 1H), 7.51 (dd, 1H), 5.82(d, 1H,), 5.63 (d, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃): 191.52, 141.20, 139.35, 136.36, 132.21, 131.41, 130.12, 128.87, 128.30, 121.15 ppm.

3.3 Synthesis of 5, 10, 15, 20-tetra-(4-nitrophenyl) porphyrin (TNPP):⁴

4-nitrobenzaldehyde (11.0 g, 73 mmol) and acetic anhydride (12 mL, 127 mmol) were dissolved in propionic acid (300 mL) with vigorous stirring under Ar. A mixture of freshly distilled pyrrole (5.0 mL, 73 mmol) in propionic acid (100 mL) was added dropwise to the reaction mixture at 120 °C. The temperature of the reaction was raised to 140 °C with constant stirring upto 2 h. Prolonged heating causes formation of unwanted material. Hence, the reaction was cooed to room temperature and the mixture was refrigerated overnight, and then the resulted precipitate was collected by filtration and washed with methanol (100 mL × 5) and deionized water (100 mL × 5). Next, the obtained dark solid was dissolved in pyridine (80 mL) and refluxed for 1 h. After cooling down, the system was refrigerated overnight. The desired purple product (TNPP) was obtained by filtering, washing with the mixture of methanol/acetone and vacuum drying (yield, 35 %). ¹H NMR (500 MHz, d_6 -DMSO) δ : 8.85 (s, 8H; C-H), 8.29 (d, 8H; Ar-H), 8.18(d, 8H; Ar-H), -2.65(s, 2H; pyrrole NH) ppm.

3.4 Synthesis of 5, 10, 15, 20-tetra-(4-aminophenyl) porphyrin (TAPP):⁴

To a mixture of TNPP (1.8 g) in concentrated hydrochloric acid (75 mL), a solution of SnCl2 (7.0 g, 29 mmol) in 20 mL of concentrated hydrochloric acid was dropwise added under Ar atmosphere. After stirring at room temperature for 3 h, the reaction mixture was heated to 80 °C for 5 h. The reaction was cooled down to room temperature and then chilled to 0 °C. Then the mixture was neutralized with ammonium hydroxide at 0 °C, and the green solid was obtained via vacuum filtration followed by dispersion in sodium hydroxide aqueous (200 mL, 5 %). Finally, the raw product was purified by Soxhlet extraction with chloroform to give purple TAPP (yield, 78 %). ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 8H, pyrrole ring), 7.98 (d, J = 8.2 Hz, 8H, ArH), 7.06 (d, J = 8.2 Hz, 8H, ArH), 4.03 (s, 8H, NH2), -2.71 (s, 2H,pyrrole NH).

3.5 Synthesis of PTF photocatalyst: TAPP (1eq, 0.5mmol) and VBD (0.5 eq, 0.5 mmol) were dissolved in nitrobenzene (25 mL) with sonication for 20 min. The solution was filtered through 0.5 μ m PTTF microfilter to get a clear nitrobenzene solution. To a closed container, with the filtered nitrobenzene solution of TAPP and VBD was layered glyoxal (30% in water, 1.5 mmol) in deionized water (25 mL). The container was kept in a preheated oven at 51°C for desired time. The formation of thin film was observed at the interface of the two liquids. The film was harvested by removing the top layer and transferring the film on desired substrate.



Scheme S1: (a) Interfacial synthesis of PTF thin film (b) PTF thin film transferred on different substrates.

4. Experimental Procedures

4.1. Photoelectrochemical measurements: Photoelectrochemical measurements were carried out in a three-armed cell consisting of reference (Ag/AgCl, BASI, MF-2063 RE-5), working (CCG-IP photoanode) and Platinum wire (Part Number: CHI115) counter electrodes using a Electrochemical analyzer (CHI Instruments 1100A). 0.1 M NaCl solution was used as a redox couple/electrolyte. Newport solar simulator (69911) was used as a light source. Light intensity was measured by VSLI standard incorporated Oriel P/N 91150V.

4.2. Standard procedure for photocatalytic dehalogenation of α **-bromoacetophenones:** The photochemical reductive dehalogenation of bromoacetophenones was performed in a quartz reactor

under an inert atmosphere at room temperature, using simulated solar light (Newport Instruments, USA) with an 450nm cutoff filter (AM 1.5). The photocatalysis was carried out as follows. The quartz reactor consisted of α -bromoacetophenone (0.4 mmol), hantzsch ester (0.44 mmol), DIEPA (0.9 mmol) and PTF photocatalyst (1 x 3 cm²) in anhydrous acetonitrile (3 mL). The reactor was initially allowed to equilibrate in dark for 30 minutes with argon purging, following which it was exposed to visible light (1 sun) until completion of reaction. The completion of reaction was monitored vial thin layer chromatography (hexane: ethyl acetate. 8:2). After photocatalysis, the thin film was removed, and the reaction mixture was filtered through 0.4 μ m PTF micro filter to remove any solid residue. The mixture was dried and column chromatographed on silica gel to obtain corresponding acetophenones.

Acetophenone (AA₁): The reaction was performed according to standard reaction procedure. 2-bromoacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.99 – 7.92 (m, 2H), 7.56 (ddd, *J* = 7.8, 4.7, 1.6 Hz, 1H), 7.46 (td, *J* = 7.7, 2.4 Hz, 2H), 2.60 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 198.10, 137.14, 133.08, 128.56, 128.28, 26.56.

4-chloroacetophenone (AA₂): The reaction was performed according to standard reaction procedure. 2-bromo-3'-chloroacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 2.59 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.81, 139.57, 135.46, 129.73, 128.90, 26.55.

3-chloroacetophenone (AA₃): The reaction was performed according to standard reaction procedure. 2-bromo-3'-chloroacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (t, *J* = 1.9 Hz, 1H), 7.82 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.0, 2.3, 1.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 2.58 (d, *J* = 1.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.61, 138.61, 134.89, 132.98, 129.92, 128.35, 126.40, 26.58.

3-methoxyacetophenone (AA₄): The reaction was performed according to standard reaction procedure. 2-bromo-4'-methoxyacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.54 (ddt, *J* = 7.8, 2.7, 1.3 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.37 (td, *J* = 7.9, 2.8 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.85 (s, 3H), 2.59 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.94, 159.82, 138.50, 129.57, 121.11, 119.58, 112.39, 55.43, 26.71.

4-methoxyacetophenone (AA₅): The reaction was performed according to standard reaction procedure. 2-bromo-4'-methoxyacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 190.72, 163.33, 141.01, 132.78, 113.69, 55.02, 30.66.

4-bromoacetophenone (AA₆): The reaction was performed according to standard reaction procedure. 2,4'-bromoacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 3H), 2.59 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.10, 164.46, 131.88, 129.83, 116.39, 27.92.

4-nitroacetophenone (AA₇): The reaction was performed according to standard reaction procedure. 2-bromo-4'nitroacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.65 – 7.58 (m, 1H), 7.47 – 7.42 (m, 1H), 2.56 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.80, 138.01, 134.23, 130.65, 127.36, 124.37, 30.15.

3-nitroacetophenone (AA₈): The reaction was performed according to standard reaction procedure. 2-bromo-3'nitroacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). Isolated yield: 75 mg as light yellow crystalline solid. ¹H NMR (500 MHz, CDCl₃) δ 8.77 (t, *J* = 2.0 Hz, 1H), 8.43

(ddd, J = 8.2, 2.4, 1.1 Hz, 1H), 8.30 (dt, J = 7.7, 1.4 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 2.70 (d, J = 1.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 195.65, 138.28, 133.77, 129.92, 127.42, 123.24, 26.72.

2-nitroacetophenone (AA₉): The reaction was performed according to standard reaction procedure. 2-bromo-2'nitroacetophenone (0.4 mmol), Hantzsch ester (0.44mmol), DIEPA (0.9 mmol). Isolated yield: 85mg as Off white crystalline solid. ¹H NMR (500 MHz, CDCl₃) δ 8.32 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 2.69 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.30, 152.35, 141.41, 129.32, 123.86, 26.97.

4.3. Photocatalytic NADH Production: The photochemical regeneration of NADH was performed within a quartz reactor under an inert atmosphere at room temperature, using simulated solar light (Newport Instruments, USA) with an air mass filter (AM 1.5). The photocatalytic regeneration of NADH was carried out as follows. The reaction was performed in a quartz reactor. The reaction consisted of β –NAD⁺ (1.24 µmol), rhodium complex **Rh** (0.62 µmol), ascorbic acid (0.1 mmol) and PTF photocatalyst (1 x 3 cm²) in 3.1 mL of sodium phosphate buffer (100 mM, pH 7.0). The reactor was initially allowed to equilibrate in dark for 30 minutes, following which it was exposed to visible light (1 sun). The regeneration of NADH was monitored by UV-vis spectrophotometer (UV-1800, Shimadzu). The NADH displays absorption maxima at 340 nm with an extinction coefficient of 6220 M⁻¹ cm⁻¹. During the illumination, the concentration of NADH was estimated by measuring the absorbance of the diluted reaction system at 340 nm.

4.4. The artificial photosynthesis of formic acid from CO₂: The artificial photosynthesis of formic acid from CO2 was also performed within a quartz reactor at room temperature, using simulated solar light (Newport Instruments, USA) with an air mass filter (AM 1.5). The reaction consisted of PTF photocatalyst ($1 \times 3 \text{ cm}^2$), β –NAD⁺ (1.24 µmol), rhodium complex **Rh** (0.62 µmol) and 3 units of formate dehydrogenase, in 3.1 mL of sodium phosphate buffer (100 mM, pH 7.0) with ascorbic acid (0.1 mmol) in the presence of CO₂ (flow rate: 0.5 mL/min). After bubbling CO₂ for 30 minutes in the absence of light (light off), the reactor was exposed to visible light (light on). The amount of formic acid was detected by lon chromatography⁵ (The Metrohm Eco IC System, Metrohm AG Herisau, Switzerland) with conductometric detector, and column: Metrosep A Supp 5-150/4.0 (length: 150.0mm; ID:4.0mm.⁵

S. No.	Interfacial Reaction Time (min)	Thickness of film (nm)
1.	1	97 nm
2.	5	215 nm
3.	15	350 nm
4.	30	560 nm
5.	60	1.45 μm
6.	720	8.45 μm

Table S1: Effect of interfacial reaction time on the thickness of PTF as analyzed by SEM analysis

Photocatalys	$\lambda_{_{abs}}^{}^{a}$ (nm)	Optical gap ^b (eV)	τ_{avg}^{c} (ns)	E _{vb} ^d (eV)	E _{cb} ^e (eV)
PTF-1min	500	2.43	2.99	-5.27	-2.92
PTF-15min	520	2.4	7.90	-5.47	-3.07
PTF-1h	509	2.45	1.68	-5.14	-2.67
PTF-12h	530	2.3	0.96	_f	_f

Table S2: Electronic properties of PTF photocatalysts.

^aUV-vis absorption edge

^bDetermined from the Kubelka-Munk-transformed reflectance spectra.

^cAverage fluorescence lifetime recorded upon excitation at λ exc = 505 nm. ^dThese values are determined from UPS with excitation energy He I, 21.22 eV . ^eThese values are determined from UPS and optical gap with respect to vacuum level ^fThe UPS data for PTF-12h film could not be estimated due to its high thickness.



Scheme S2: valence band (VB) and conduction band (CB) positions of PTF photocatalyst.

Table S3: Emission decay analysis for PTF photocatalysts.

Photocatalyst	$ au_1$ (ns)	Rel (%)	$ au_2$ (ns)	Rel (%)	au(ns)	χ ²
PTF-1min	1.95	97.73	3.32	2.27	2.99	1.00
PTF-15min	2.63	96.87	5.75	3.13	7.90	1.01
PTF-1h	1.69	98.35	3.95	1.65	1.68	1.12
PTF-12h	1.39	98.03	3.25	1.97	0.96	0.98

The time-resolved PL decay curves were fitted with the following eq 1: ^{17,18}

fit = A + B₁ exp[-t/
$$\tau_1$$
]+ B₂ exp[-t/ τ_2] (1)

Where A, B₁, and B₂ are constants obtained after fitting the corresponding PL decay curve. From this equation, a fast (τ_1) and a slow (τ_2) decay component was obtained. These data were then fed into eq 2 to calculate the intensity average lifetime (τ) for all the PTF photocatalyst.⁵¹⁷

$$\tau = [B_1 \tau_1^2 + B_2 \tau_2^2] / [B_1 \tau_1 + B_2 \tau_2]$$
(2)

 Table S4: Reaction optimization.



Entry	Photocatalyst	Solvent	Conversion (%)
1	PTF-15 min		99.9
2.	No Photocatalyst	CH CN	-
3.	PTF-15 ^ª min		5
4.	PTF-15 ^b min	CH ₃ CN	-
5.	PTF-15 [°] min	CH ₃ CN	-
6.	PTF-15 ^d min	CH ₃ CN	10
7.	PTF-15 min	C ₂ H ₅ OH	75
8.	PTF-15 min	DCM	45
9.	PTF-15 min	DMF	80

Reaction conditions: PTF-15min (1 x 3 cm²) photocatalyst, α-bromoacetophenone (0.4 mmol),

hantzsch ester (0.44 mmol), DIEPA (0.9 mmol), anhydrous acetonitrile (3 mL). ^a in dark, ^b in absence of hantzsch ester, ^c in absence of DIEPA, ^d in presence of TEMPO. All the light reactions were carried out for 3h of visible light irradiation.

Photocatalys t	Solven t	Light Source	Time	Yiel d (%)	Recyclabilit y	Referenc e
PTF Photocatalys t	CH₃CN	Xenon lamp with a 420 nm cut-off-filter (100mW/cm²)	2h	99	10 cycles	Our Work
OH-TFP-TTA COF	CH₃CN	30 W green LED (530 nm)	18h	90	4 cycles	12
B-FL2-BBT	DMF	23 W household lamp	4h	93	5 cycles	13
Cz-POF-1	CH₃CN	14 W compact Fluorescent Lamp	24h	98	5 cycles	14
COF-JLU22	CH₃CN	White LED	8h	74	5 cycles	15
B-BT/Glass fiber	DMF	White LED (>420nm)	-	-	5 cycles	16

Table S5: A Comparative literature survey for Photocatalytic reductive dehalogenation of α -bromoacetophenones under visible light illumination.

Table S6: A Comparative literature survey for Photocatalytic integrated enzyme system for CO_2 to solar fuel conversion.

S. No.	Photocatalyst	Topdown/ bottom up	NADH regeneration (%)	Formic acid (µmol)	Time (h)	Ref.
1.	PTF-15 min	Free standing	98.45	334.1	2	Our Work
2.	Ru-Nu-1006	-	28	303.7	24	6
3.	T-COF-2	-	74	NA	2	7
4.	N-GDY	Top-down	30	NA	2	8
5.	GFPC1	bottom up	91.8	228.6	2	9
6.	3DAP	Drop casting	91.09	225.25	2	10
7.	CTF	Drop casting	75.88	204.14	2	11



Scheme S3: Synthetic Scope of reductive dehalogenation of α -bromoacetophenones for the synthesis of important Drug molecules.



Scheme S4: Mechanistic illustration for Photocatalytic reductive dehalogenation of α -

bromoacetophenones under visible light illumination.



Figure S1. FE-SEM image of PTF photocatalyst under different magnifications at a concentration of (a & b) 0.75 M and (c) 1M concentration of TPPA (d) Powder PTF photocatalyst.



Figure S2. XRD spectra of PTF-15min photocatalyst.



Figure S3. FTIR spectra of PTF-15min photocatalyst and VBD.



Figure S4. FTIR spectra of TAPP.



Figure S5. XPS spectra of PTF photocatalyst for different N1s species.



Figure S6. UV-Visible absorbance of TAPP and VBC in chloroform (1 x 10^{-4} M).



Figure S7. A comparison of NADH regeneration and formic acid production by PTF-15min photocatalyst under standard reaction conditions.



Figure S8. CO₂ adsorption isotherm for PTFs photocatalyst at 308 K.





Figure S9. Recyclability of 1 x 3 cm² PTF-15min photocatalyst for (a) NADH Regeneration and (b) formic acid production upto six cycles. The photocatalysis was carried out using 1 x 3 cm² film photocatalyst by illuminating the quartz reactor containing β –NAD⁺ (1.24 µmol), Rhodium complex Rh (0.62 µmol) and AsA (0.1 mmol) in 3.1 ml of 0.1 M sodium phosphate (NaH₂PO₄-Na₂HPO₄) buffer (pH ~ 7.0). The formic acid production was carried out in presence of 3U of FDH. A solar stimulator stimulated @AM 1.5, 1Sun, (Newport Instruments, USA) was used as a light source. The film was washed with water (25 x 3 mL) and acetone (25 x 3 mL) and dried for 12 h in vacuum oven for next cycle.





Figure S10. FESEM image of PTF-15min (a) before and (b) after photocatalysis.



Figure S11. FTIR spectra of PTF-15 before (red) and after photocatalysis (black).



Figure S12. The cyclic voltammograms of PTF-15min photocatalyst in phosphate buffer in presence of Rh complex with and without NAD⁺.



Figure S13. GC-MS spectrum of formic acid (H¹³COOH) obtained from ¹³CO₂ using PTF-15min photocatalyst-biocatalyst integrated artificial photosynthetic system under standard reaction conditions.



Figure S14: PTF-15min photocatalyzed reductive dehalogenation of α -bromoacetophenones for 10 runs. Reaction conditions: PTF PTF-15min photocatalyst (1 x 3 cm²), α -bromoacetophenone (0.4 mmol), hantzsch ester (0.44 mmol), DIEPA (0.9 mmol), anhydrous acetonitrile (3 mL). The p hotocatalyst film was suspended in chloroform and ethyl acetate successively and finally in acetone for 20 mins with stirring. Finally after rinsing it with water and acetone, it was dri ed in oven at 120 °C overnight before reuse.



Figure S16: ¹³C NMR of 2-Bromobenzene-1,4-Dicarbaldehyde.



Figure S17. ¹H NMR of 2-vinylbenzene-1,4-Dicarbaldehyde.



Figure S18. ¹³C NMR of 2-vinylbenzene-1,4-Dicarbaldehyde.

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