

## Electronic Supporting Information

### **Se<sub>in</sub>-EY Marvels: Effortless Elegance in Crafting Flexible Film Photocatalysts for Formic Acid Production from CO<sub>2</sub> and Cyclization of Thioamides in the Air's Embrace**

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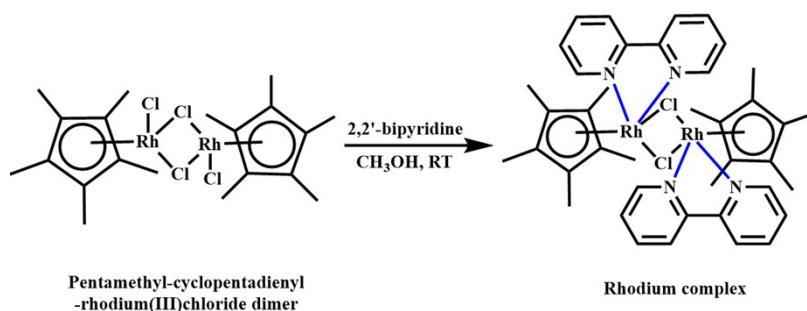
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## 1. Instruments and Measurements

UV-Visible (UV-Visible) spectroscopy were recorded on Shimadzu UV-1800 spectrometer. Fourier transform infrared spectroscopy (FTIR) spectroscopy were obtained on a Nicole 6700 (made by Thermo Scientific, USA) spectrometer using the KBr pellet support. Powder X-ray diffractometer (Bruker, AXS D8 Advance X-ray diffractometer and Cu  $K\alpha$  radiation) was used. Scanning electron microscope (SEM) images were obtained on a FET Phillips instrument [Model No. 200k VLAB6, (FEL TECNAI G2-20S- Twin)] operated at ( $\lambda = 0.15406 \text{ nm}$ ) 200 kv. Transmission electron microscope (TEM) images were obtained on a FET Phillips instrument [Model No. 200k VLAB6, (FEL TECNAI G2- S3 20S-Twin)] operated at 200 kV. Cyclic Voltammetry, Tafel plot, EIS were performed on (CHI608E, 220V) instrument. TGA were recorded on (TGA) was carried out on TA Instruments Q500 instrument over a range of 25-800 °C with a heating rate of 5°C min<sup>-1</sup>. <sup>1</sup>H NMR spectra was recorded on a Bruker AVANCE II + 300 MHz spectrometer with tetramethylsilane (TMS;  $\delta = 0$ ) as internal standard. HPLC was recorded on LC-20AP, SHIMADZU. XPS (X-ray photon electron spectroscopy) were recorded on Escalab 250Xi, Thermo Fisher, America. GC-MS spectra recorded on Agilent 6890N gas chromatograph.

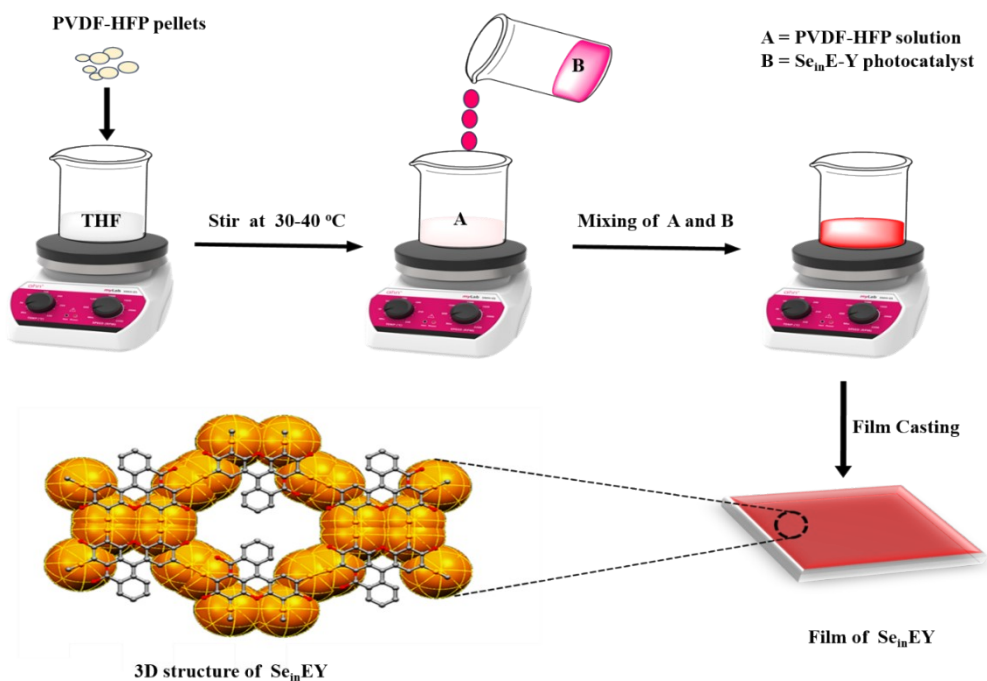
## 2. Synthesis of Rhodium complex $[\text{Rh} = \text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]^+$

First, 5 mL of distilled methanol was used to dissolve 25 mg of Rh compound ( $[\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_2]$ ) in a  $\text{N}_2$  environment. As a result, 13 mg of 2,2'-bipyridyl (2 eq.) was added to the above solution and stirred at room temperature in the dark. A yellow precipitate formed after adding diethyl ether. In the final step, the obtained product is filtered and dried at room temperature under  $\text{N}_2$  environment. For the synthesis of the Rhodium complex (Rh), the described procedure was followed.<sup>1</sup>



**Fig. S1** Synthesis of Rhodium complex.

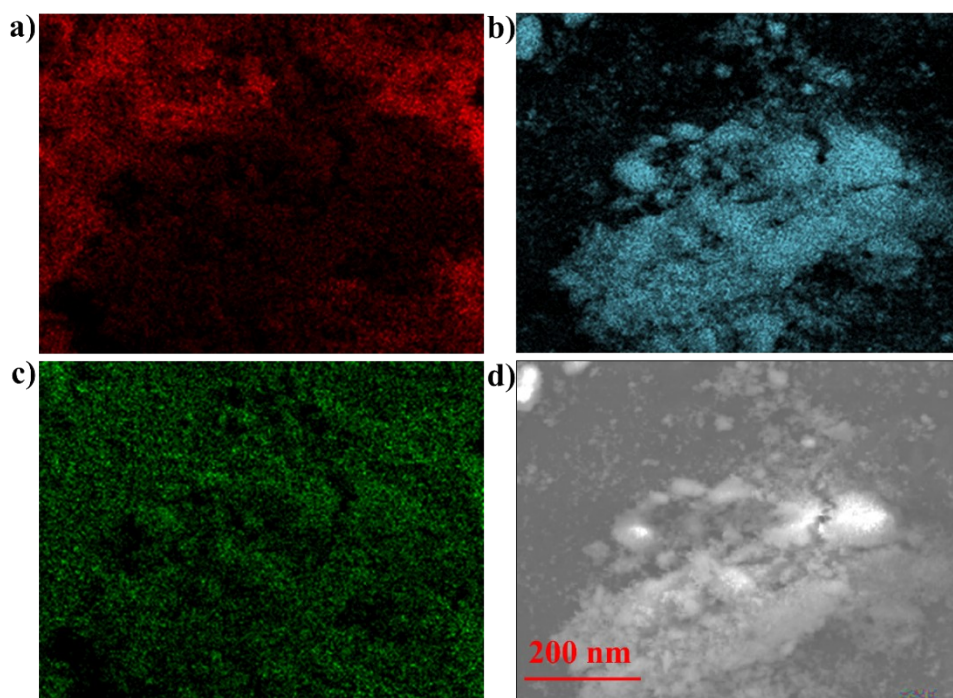
### 3. Preparation of flexible film of $\text{Se}_{\text{in}}\text{-EY}$ photocatalyst



**Fig. S2** Diagrammatic illustration for the Synthesis of flexible film of  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst.

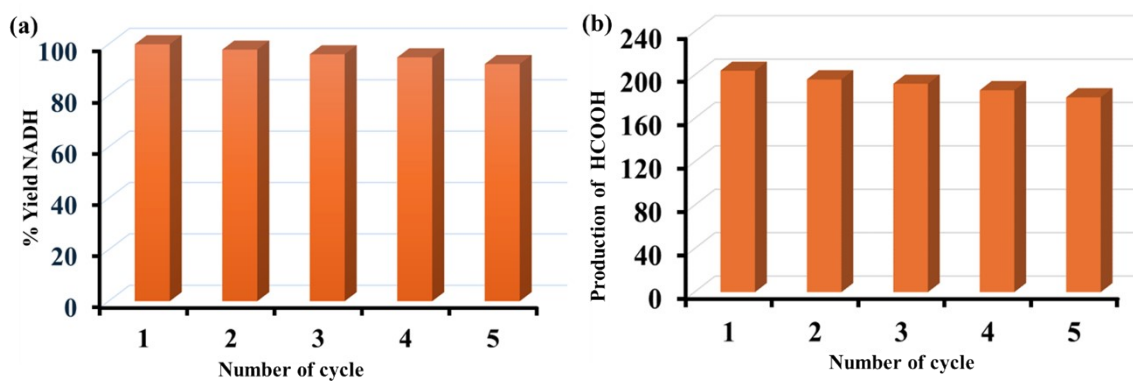
Initially, in the tetrahydrofuran (THF) solvent, (vinylidene fluoride-co-hexafluoropropylene) polymer pellets were added. After 2-3 hours, the PVDF-PHF pellets get dissolved into the tetrahydrofuran (THF) to become the solvent thick. In the meantime,  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst dissolve in chloroform to make solution B. This solution B we then added into the earlier prepared thick solution A and stir for a minute. Now, when these two gets added together formed a layer. Over the period, the chloroform was gradually evaporated leaving behind the  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst to settle down with the dissolved polymer. It was converted into a film after being dried. Eventually, we took out the flexible film of  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst.

#### 4. Elemental mapping of EY along with SEM



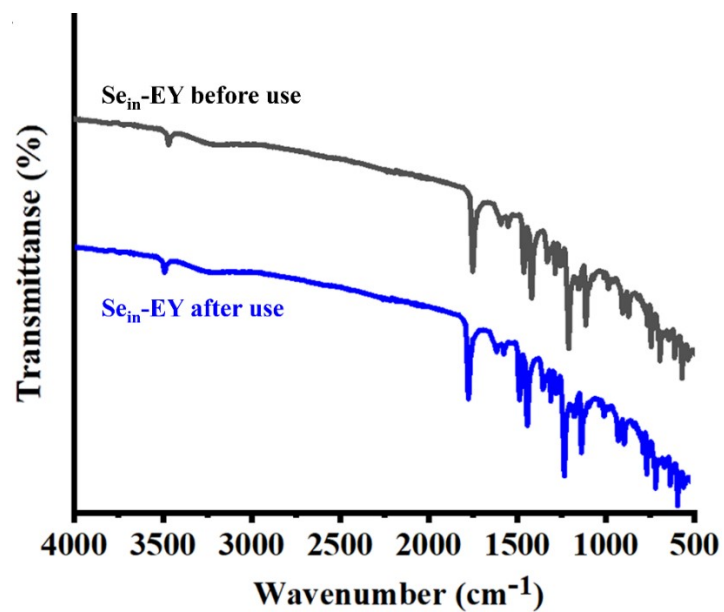
**Fig S3.** Elemental mapping images of (a) Carbon of EY, (b) Bromine of EY, (c) Oxygen of EY, and (d) SEM image of EY monomer.

#### 5. Cyclic stability and reusability test



**Fig. S4** Five times cyclic stability experiments for 1,4-NADH photo regeneration and formic acid (HCOOH) production from CO<sub>2</sub>. The reaction medium contains (a) β-NAD<sup>+</sup> (1.24 μM), AsA (1.24 μM), Rh (0.62 μM), and the Se<sub>in</sub>-EY (1x1cm<sup>2</sup>) film photocatalyst in 3.1 mL NPB (100 mM, pH 7.0). (b) Formic acid production from CO<sub>2</sub> under solar light [β-NAD<sup>+</sup> (1.24 μM),

AsA (1.24  $\mu\text{M}$ ), Rh (0.62  $\mu\text{M}$ ), and the  $\text{Se}_{\text{in}}\text{-EY}$  ( $1 \times 1 \text{ cm}^2$ ) film photocatalyst in 3.1 mL NPB (100 mM, pH 7.0), FDH (3 units).



**Fig.S5** The reusability and chemical stability of the  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst through FT-IR spectra.

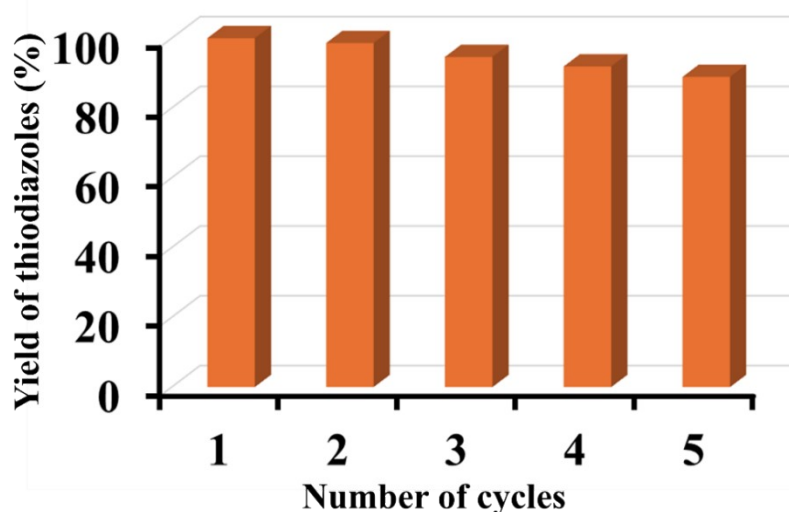
**7. A Comparative study of reported literature with Se<sub>in</sub>-EY photocatalyst for NADH regeneration and formic acid synthesis from CO<sub>2</sub>**

S.N.	Photocatalyst	Method	Time	%1,4-NADH	Formic acid (μM)	Reference
1.	Hierarchical Cu pillar electrode	Electrochemical	6h	---	13.17	4
2.	COF-367-Coll	Photochemical	8h	---	3.89	5
3.	RB/Si-NaYF <sub>4</sub> : Yb,Er	Photochemical	1h	18.86%	---	6
4.	W <sub>2</sub> Fe <sub>4</sub> Ta <sub>2</sub> O <sub>17</sub>	Photochemical	14h	60	---	7
5.	CdTe nanocrystals	Photochemical	2h	55	---	8
6.	CaLa <sub>4</sub> Ti <sub>4</sub> O <sub>15</sub>	Electrochemical	1h	---	1.8	9
7.	RuP/C <sub>3</sub> N <sub>4</sub>	Photochemical	1h	---	8.8	10
8.	PANi-ClFDH	Electrochemical	1h	---	1.42	11
9.	Fmoc-FF/g-CN	Photochemical	3h	62.7	---	12
10.	Se <sub>in</sub> -EY	Photochemical	2 h	83.56%	204	Our work

**Table S1:** Comparative studies for NADH photoregeneration and formic acid production from CO<sub>2</sub>.

### 8. Reusability test for Se<sub>in</sub>-EY film photocatalyst for aerobic oxidative cyclization

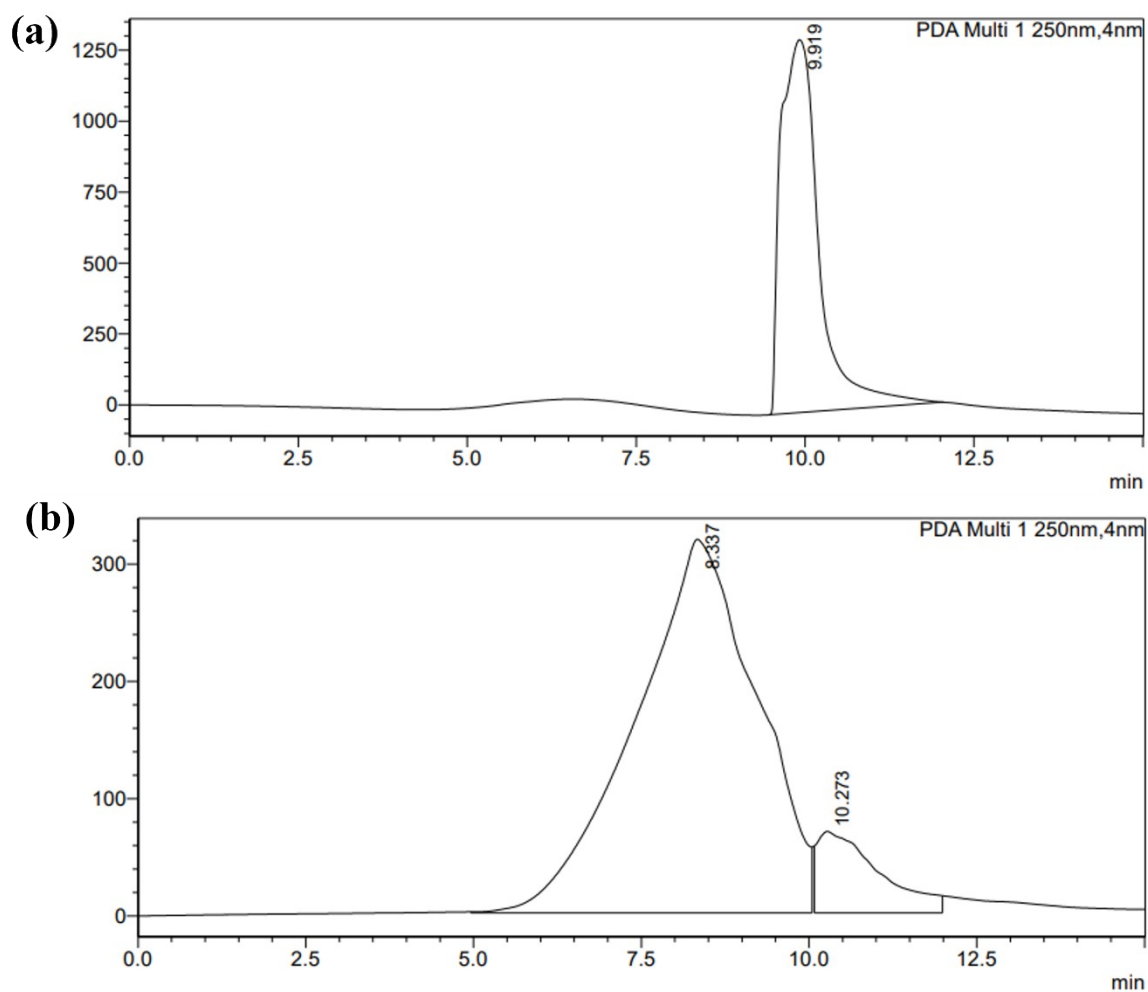
The reusability of the Se<sub>in</sub>-EY film photocatalyst was scrutinized by subjecting it to several cycles for the aerobic oxidative cyclization under solar light irradiation. As shown in table 1 (entry 2), in evaluation to the first cycle where in the Se<sub>in</sub>-EY film photocatalyst carried out 98.6% (100%) of aerobic cyclization of thioamides, and 87.5% (88.9%) was obtained in the fifth cycle (see in ESI on Fig. S6). The photocatalytic effectiveness of Se<sub>in</sub>-EY film photocatalyst remains consistent after multiple recycles, indicating its great stability. The obtain result show that the excellent reusability and stability of Se<sub>in</sub>-EY film photocatalyst. The aerobic oxidative cyclization in presence of Se<sub>in</sub>-EY photocatalyst gives high yield product in less time as compared to other reported catalyst.<sup>1,2</sup>



**Fig. S6** Reusability test of Se<sub>in</sub>-EY photocatalyst for thiobenzadiazoles synthesis by aerobic oxidative cyclization.

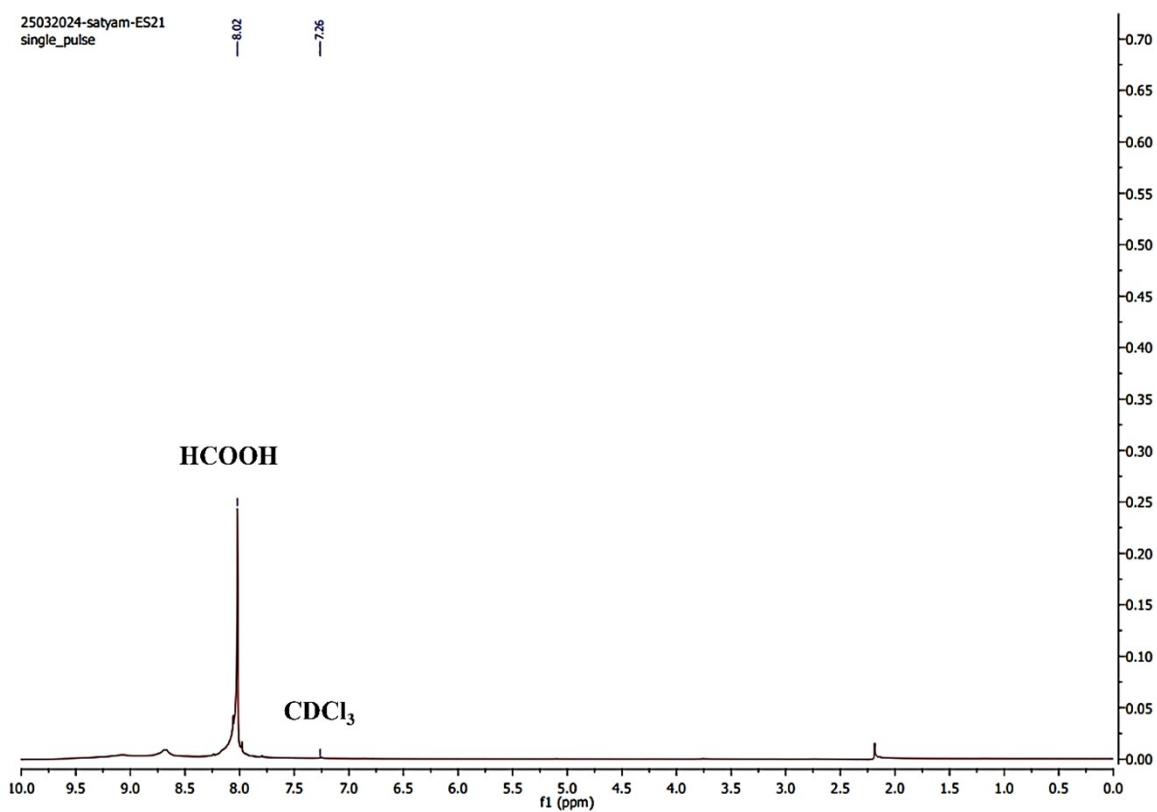
### 9. High performance liquid chromatography (HPLC)

The formic acid production was determined by HPLC. To test the required dimensions of the column, formic acid solution (50 % v/v in methanol) was run on C-18 columns of 10 cm and 25 cm length. The flow rate was maintained at 1.5 ml/min, injection volume 20 $\mu$ L and detection was carried out using UV at 250nm at ambient temperature.<sup>3</sup> HPLC Chromatogram of 50% formic acid in methanol solvent (Fig S7a) shows absorbance at 250nm with 9.919min retention time with high concentration whereas the chromatogram of production of formic acid (HCOOH) from CO<sub>2</sub> shows decreased retention time at 8.337min due to low concentration of produced formic acid via Se<sub>in</sub>-EY photocatalyst under solar light.

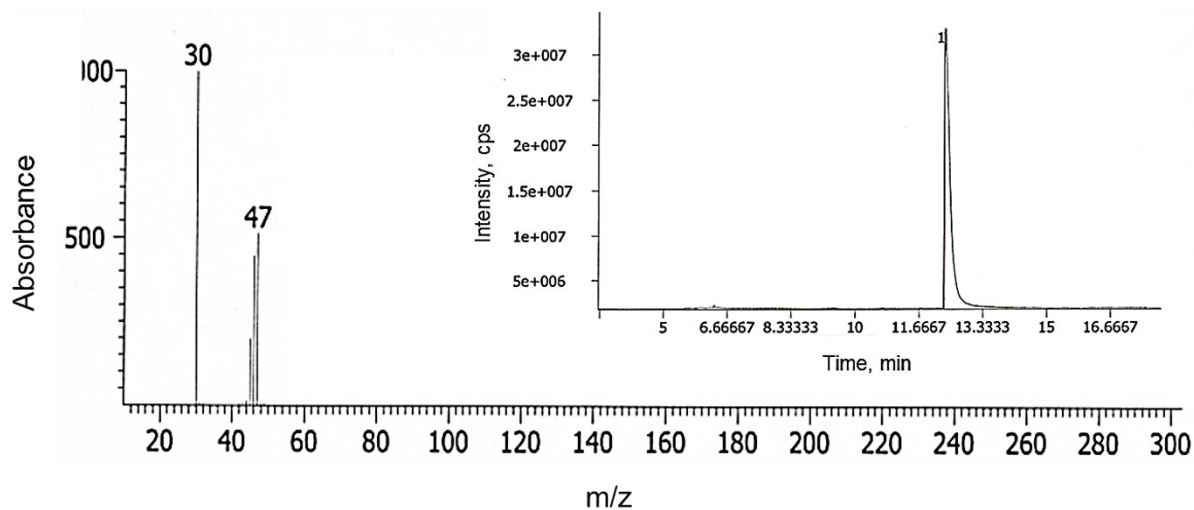


**Fig. S7** (a) HPLC Chromatogram of 50% formic acid in methanol solvent, (b) Chromatogram of production of formic acid (HCOOH) from CO<sub>2</sub> ([ $\beta$ -NAD<sup>+</sup> (1.24  $\mu$ M), AsA (1.24  $\mu$ M), Rh (0.62  $\mu$ M), and the Se<sub>in</sub>-EY (1 x 1cm<sup>2</sup>) film photocatalyst in 3.1 mL NPB (100 mM, pH 7.0), FDH (3 units)].



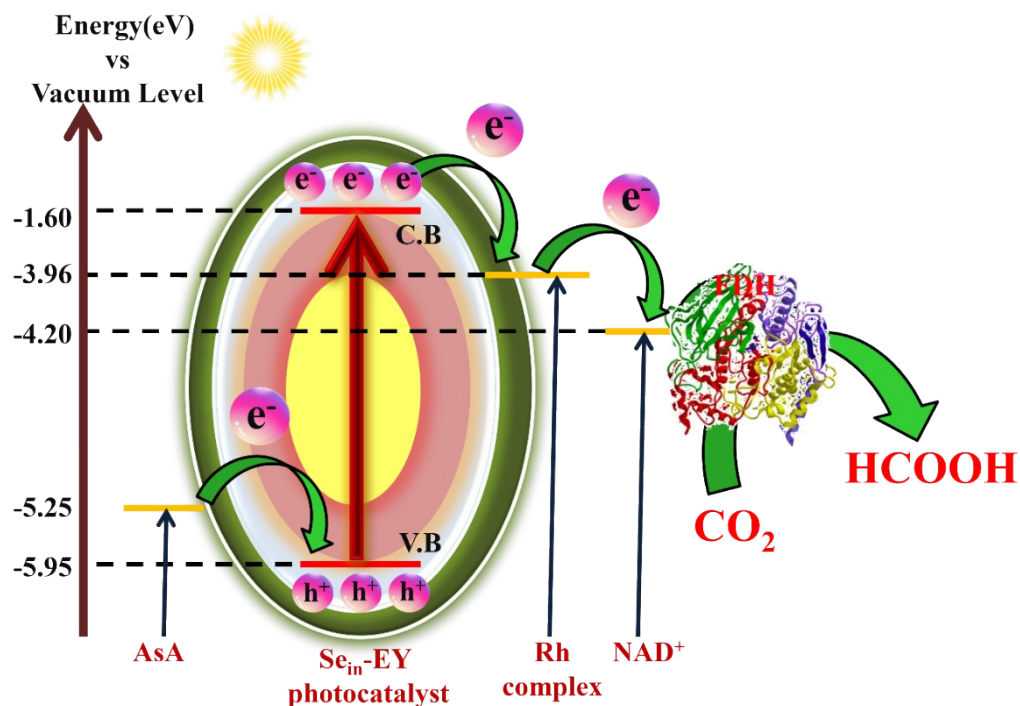
**10. Proton NMR spectra of formic acid produced by CO<sub>2</sub> reduction****<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 500 MHz) 8.02 (s, 1H), 7.26 (s, solvent)<sup>4</sup>**Fig. S8** <sup>1</sup>H-NMR spectra of HCOOH produced in CO<sub>2</sub> reduction process (CDCl<sub>3</sub> solvent, 500MHz).

### 11. GC-MS spectra of formic acid produced from CO<sub>2</sub> via isotope labelled experiment

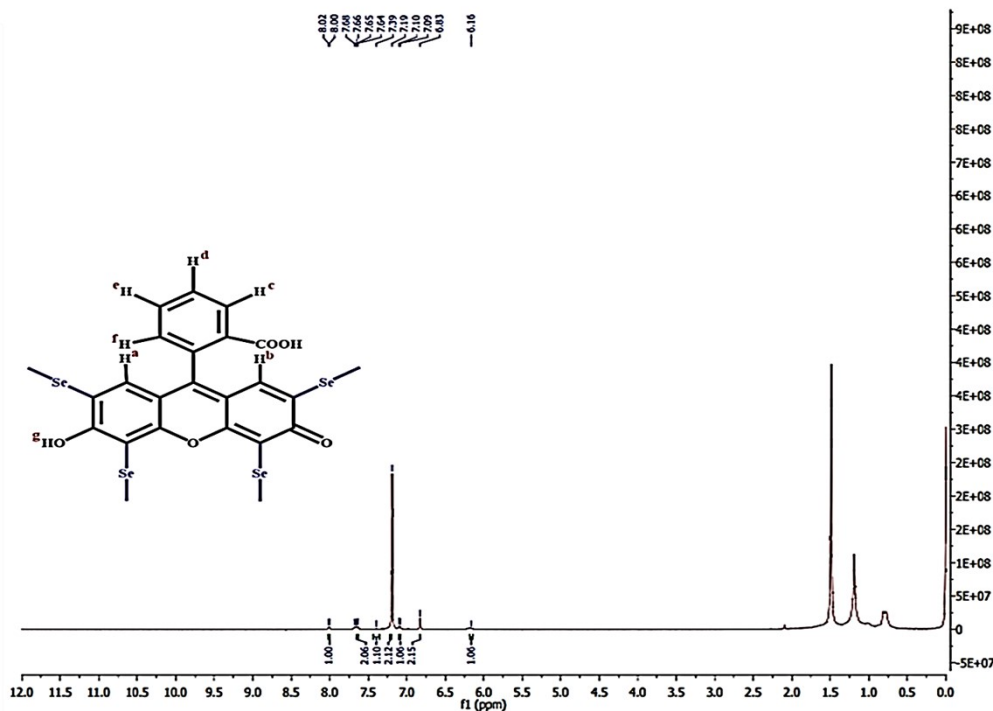


**Fig. S9** GC-MS spectra of formic acid (H<sup>13</sup>COOH) produced from <sup>13</sup>CO<sub>2</sub> via isotope labelled experiment with inset TIC chromatogram.

### 12. Plausible mechanism for CO<sub>2</sub> reduction into formic acid



**Fig. S10** Energy flow diagram of the photocatalytic pathway for possible mechanism of carbon dioxide reduction into formic acid.

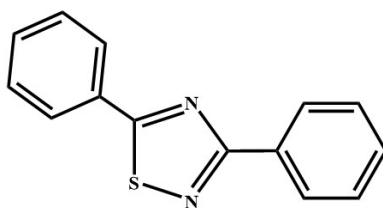
13.  $^1\text{H-NMR}$  analysis of  $\text{Se}_{\text{in}}\text{-EY}$  photocatalyst

**Fig. S11**  $^1\text{H}$  NMR spectrum of  $\text{Se}_{\text{in}}\text{-EY}$  polymeric framework photocatalyst.

#### 14. Procedure for Synthesis of 3,5-diphenyl-1,2,4-thiadiazole (2a) along with $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis

Benzothioamide **1a** (1.0 mmol), 3mL DMF was added in a 25 mL glass vial. A film of  $\text{Se}_{\text{in}}\text{-EY}$  ( $1 \times 1 \text{ cm}^2$ ) photocatalyst dipped in solution. The mixture was irradiated under a blue bulb (light source), stirring it for 2- 3 hours in aerobic conditions at room temperature (r.t.). A thin layer chromatography (TLC) was used for monitoring progress of the reaction. After completion of the reaction, film of photocatalyst removed from solution and added 5mL  $\text{H}_2\text{O}$  and extracted with EtOAc (15 mL). The organic layer solution separated and passed through magnesium sulphate ( $\text{MgSO}_4$ ) to trap moisture. The filtrate dried under reduced pressure and a solid crude product 3,5-diphenyl-1,2,4-thiadiazole **2a** was obtained. **Yield: 95%**

S11



2a

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz) 7.84-7.86 (m, 2H), 7.48-7.51 (m, 2H), 7.37-7.41 (m, 6H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz) 126.83, 127.02, 127.07, 127.30, 128.60, 128.84, 132.13, 139.25, 185.9, 190.5

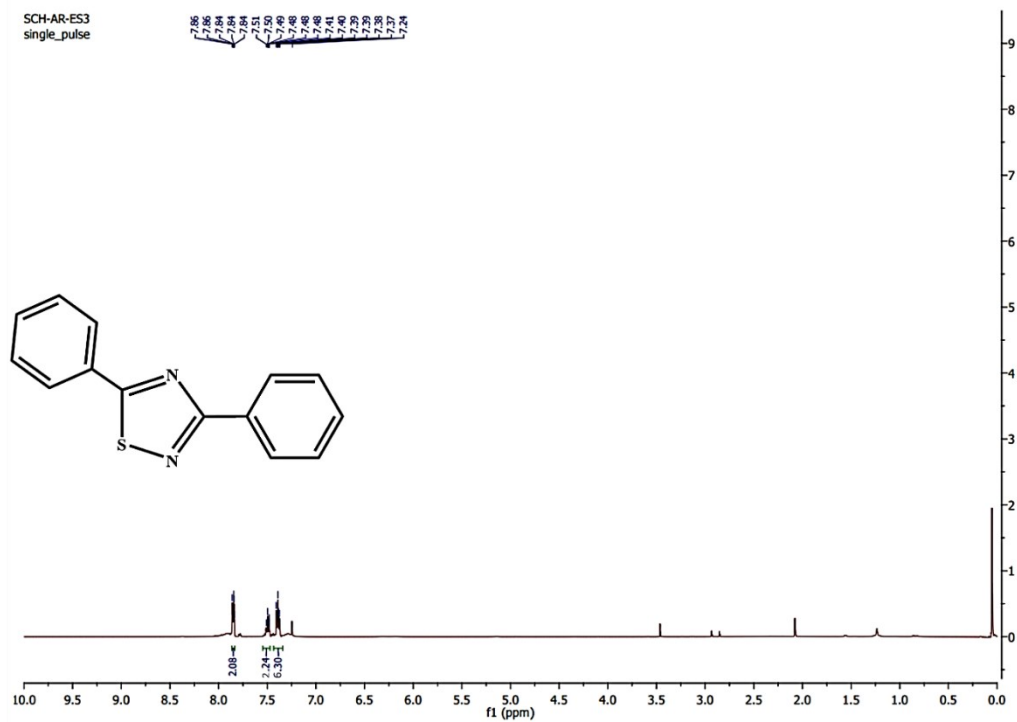
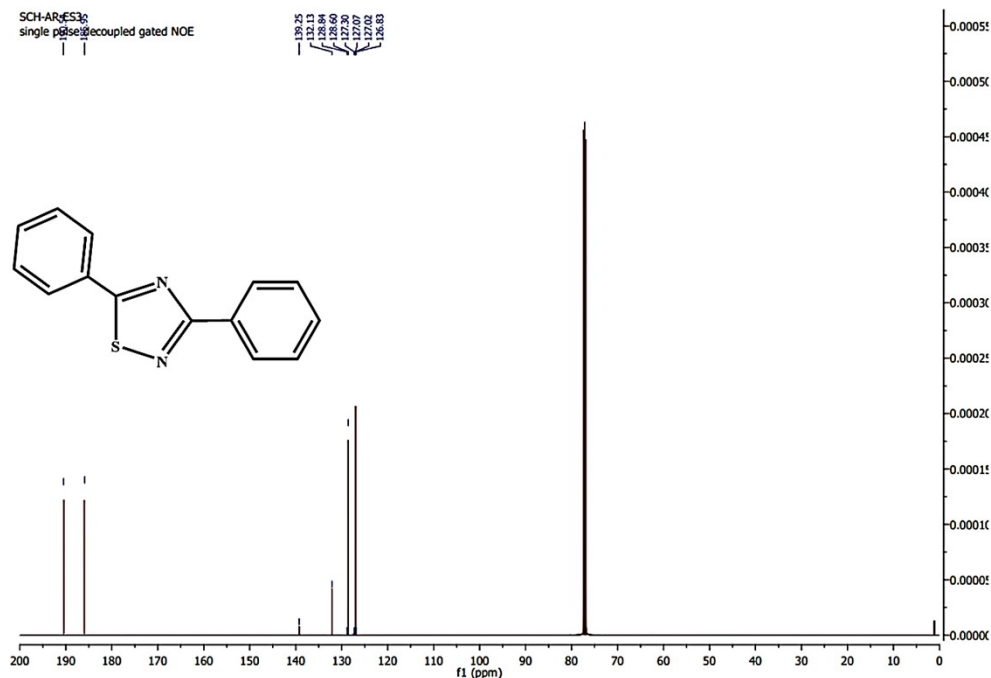


Fig.S12  $^1\text{H-NMR}$  spectra of 3,5-diphenyl-1,2,4-thiadiazole (2a).

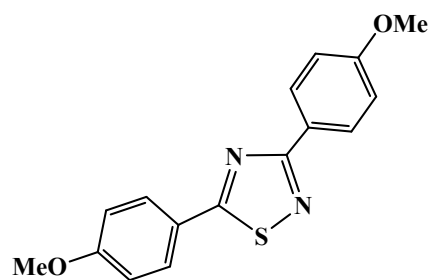


**Fig.S13**  $^{13}\text{C}$ NMR spectra of 3,5-diphenyl-1,2,4-thiadiazole (**2a**).

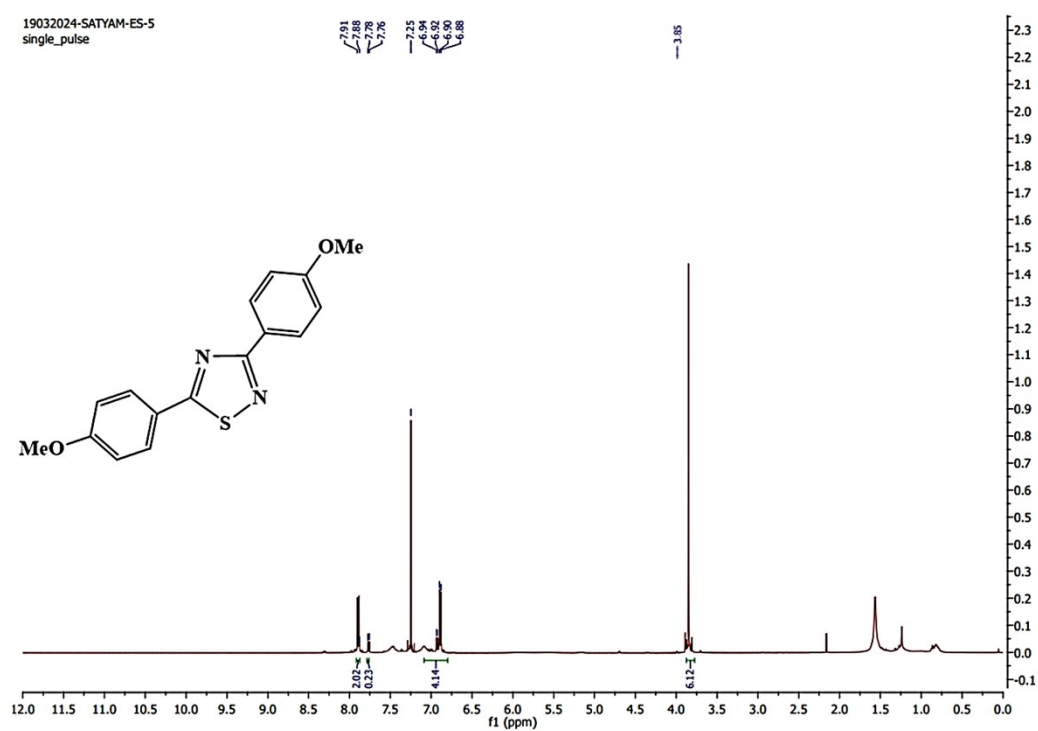
### 15. Procedure for Synthesis of 3,5-bis(4-methoxyphenyl)-1,2,4-thiadiazole (**2b**) along with $^1\text{H}$ -NMR

4-methoxybenzothioamide **1b** (1.0 mmol), 3mL DMF was added in a 25 mL glass vial. A film of  $\text{Se}_{\text{in}}$ -EY (1x1  $\text{cm}^2$ ) photocatalyst dipped in solution. The mixture was irradiated under a blue bulb (light source), stirring it for 2- 3 hours in aerobic conditions at room temperature (r.t.). A thin layer chromatography (TLC) was used for monitoring progress of the reaction. After completion of the reaction, film of photocatalyst removed from solution and added 5mL  $\text{H}_2\text{O}$  and extracted with EtOAc (15 mL). The organic layer solution separated and passed through magnesium sulphate ( $\text{MgSO}_4$ ) to trap moisture. The filtrate dried under reduced pressure and a solid crude product 3,5-bis(4-methoxyphenyl)-1,2,4-thiadiazole **2b** was obtained. **Yield: 96%**

S13



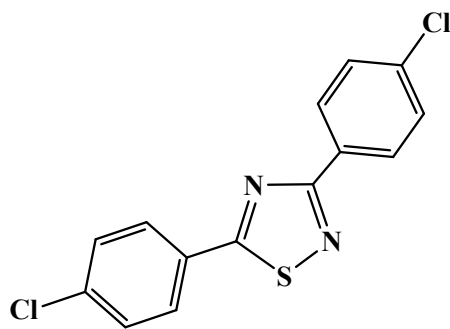
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz): 7.88-7.91 (d, 2H), 7.76-7.78 (d, 2H), 6.88-6.94 (dd, 4H), 3.85 (s, 6H)



**Fig.S14**  $^1\text{H-NMR}$  spectra of 3,5-bis(4-methoxyphenyl)-1,2,4-thiadiazole (2b).

**16. Procedure for Synthesis of 3,5-bis(4-chlorophenyl)-1,2,4-thiadiazole (2c) along with <sup>1</sup>H-NMR and <sup>13</sup>C-NMR analysis**

4-chlorobenzothioamide **1c** (1.0 mmol), 3mL DMF was added in a 25 mL glass vial. A film of Se<sub>in</sub>-EY (1x1 cm<sup>2</sup>) photocatalyst dipped in solution. The mixture was irradiated under a blue bulb (light source), stirring it for 2- 3 hours in aerobic conditions at room temperature (r.t.). A thin layer chromatography (TLC) was used for monitoring progress of the reaction. After completion of the reaction, film of photocatalyst removed from solution and added 5mL H<sub>2</sub>O and extracted with EtOAc (15 mL). The organic layer solution separated and passed through magnesium sulphate (MgSO<sub>4</sub>) to trap moisture. The filtrate dried under reduced pressure and a solid crude product 3,5-bis(4-chlorophenyl)-1,2,4-thiadiazole **2c** was obtained. **Yield: 96%**

**2c**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz) 7.79-7.80 (d, 2H), 7.71–7.73 (d, 2H), 7.34 -7. 41 (dd, 4H), 3.46(s,1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz) 128.01, 128.06,127.95, 127.96, 129.1, 129.2,133.12, 173.16, 188.27

## S15

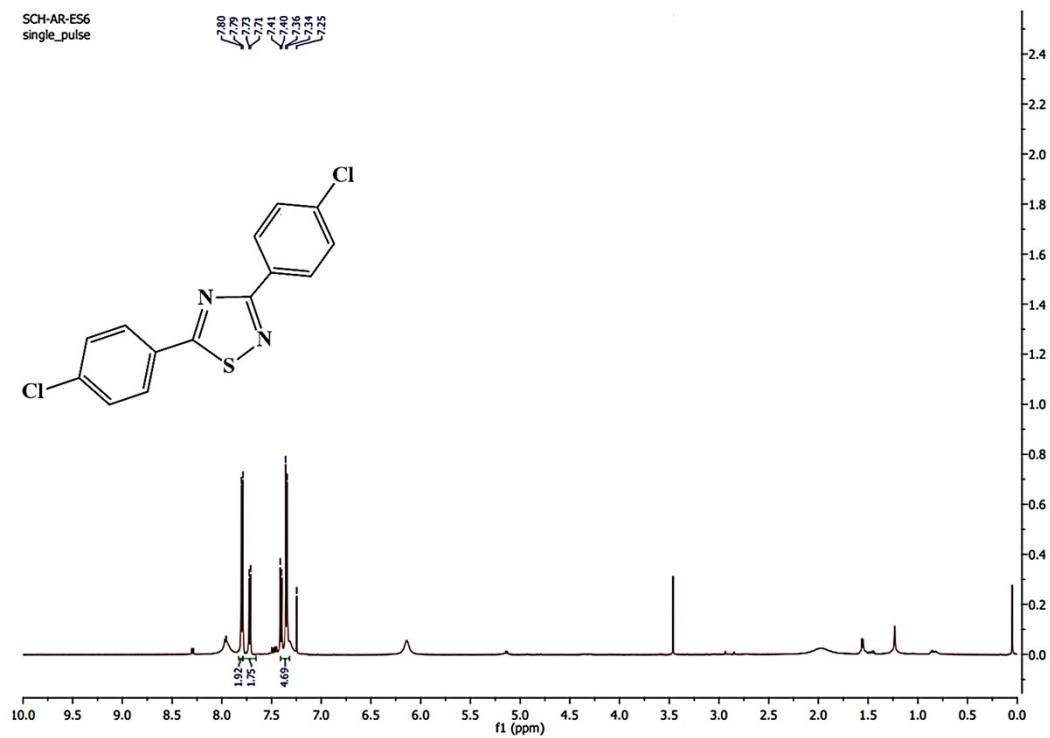


Fig.S15  $^1\text{H}$ NMR spectra of 3,5-bis(4-chlorophenyl)-1,2,4-thiadiazole (2c).

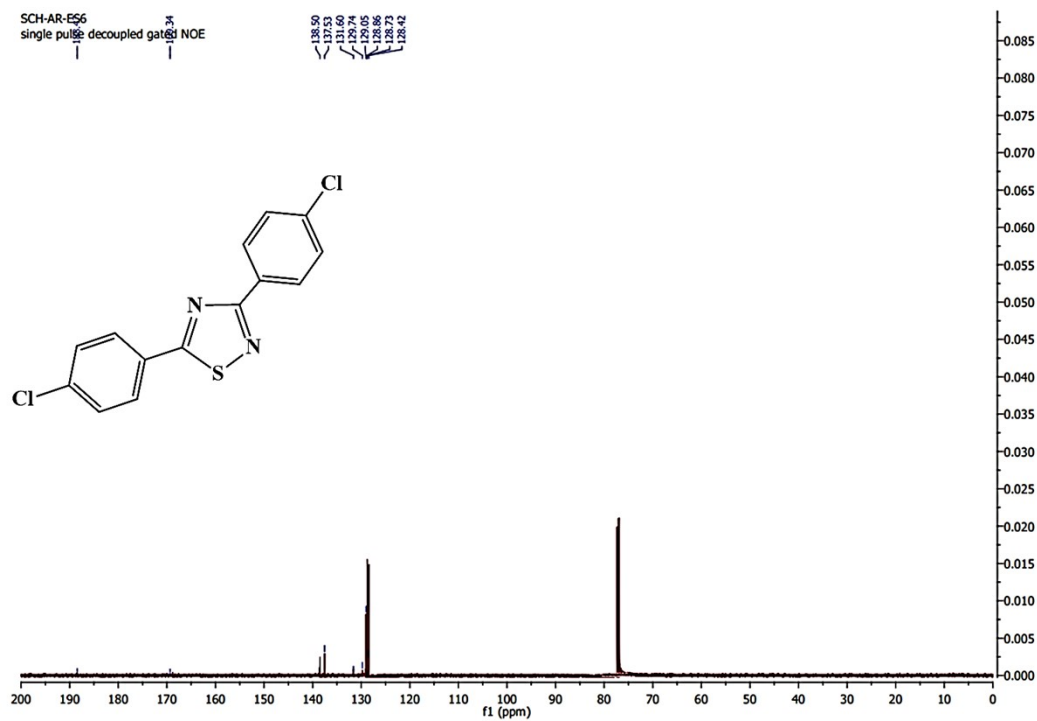
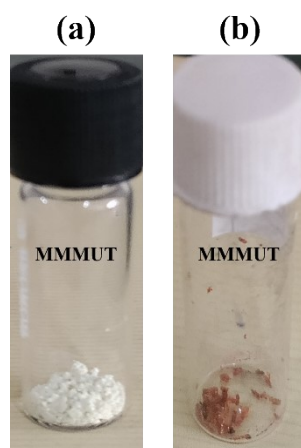
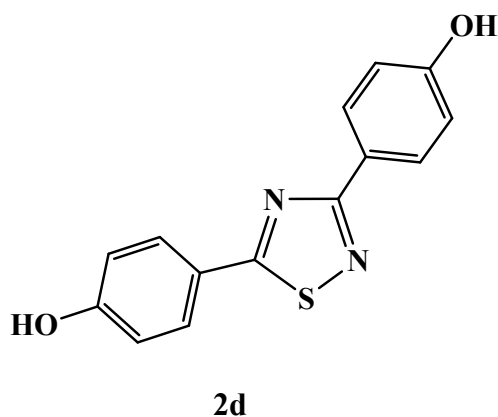


Fig.S16  $^{13}\text{C}$ NMR spectra of 3,5-bis(4-chlorophenyl)-1,2,4-thiadiazole (2c).



**17. Procedure for Synthesis of 4,4'-(1,2,4-thiadiazole-3,5-diyl) diphenol (2d)**

4-hydroxybenzothioamide **1d** (1.0 mmol), 3mL DMF was added in a 25 mL glass vial. A film of Se<sub>in</sub>-EY (1x1 cm<sup>2</sup>) photocatalyst dipped in solution. The mixture was irradiated under a blue bulb (light source), stirring it for 2- 3 hours in aerobic conditions at room temperature (r.t.). A thin layer chromatography (TLC) was used for monitoring progress of the reaction. After completion of the reaction, film of photocatalyst removed from solution and added 5mL H<sub>2</sub>O and extracted with EtOAc (15 mL). The organic layer solution separated and passed through magnesium sulphate (MgSO<sub>4</sub>) to trap moisture. The filtrate dried under reduced pressure and a solid crude product 4,4'-(1,2,4-thiadiazole-3,5-diyl) diphenol **2d** was obtained. **Yield: 98.6%**

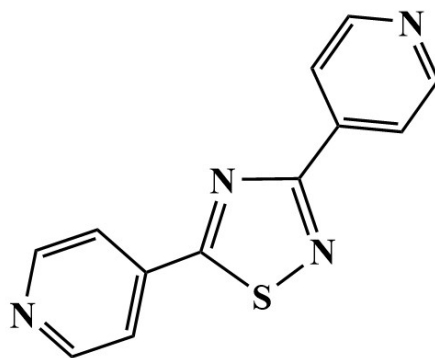


**Fig. S17** Image of (a) 4-hydroxybenzothioamide (light yellow solid) (b) 4,4'-(1,2,4-thiadiazole-3,5-diyl) diphenol (light brown solid).

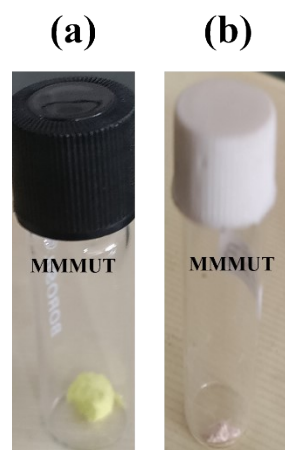
**18. Procedure for Synthesis of 3,5-di(pyridin-4-yl)-1,2,4-thiadiazole (2e)**

4-pyridine-4-carbothioamide **1e** (1.0 mmol), 3mL DMF was added in a 25 mL glass vial. A film of Se<sub>in</sub>-EY (1x1 cm<sup>2</sup>) photocatalyst dipped in solution. The mixture was irradiated under a blue bulb (light source), stirring it for 2- 3 hours in aerobic conditions at room temperature (r.t.). A thin layer chromatography (TLC) was used for monitoring progress of the reaction. After completion of the reaction, film of photocatalyst removed from solution and added 5mL H<sub>2</sub>O and extracted with EtOAc (15 mL). The organic layer solution separated and passed through magnesium sulphate (MgSO<sub>4</sub>) to trap moisture. The filtrate dried under reduced pressure and a solid crude product 3,5-di(pyridin-4-yl)-1,2,4-thiadiazole **2e** was obtained.

**Yield: 92%**



**2e**



**Fig. S18** Image of (a) 4-pyridine-4-carbothioamide (yellow solid) (b) 3,5-di(pyridin-4-yl)-1,2,4-thiadiazole (light pink).

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