Electronic Supporting Information

Natural Sunlight Harvesting Benzothiadiazole-based Molecular Photocatalyst for H_2O_2 Production: Recyclable Homogeneous Biphasic System

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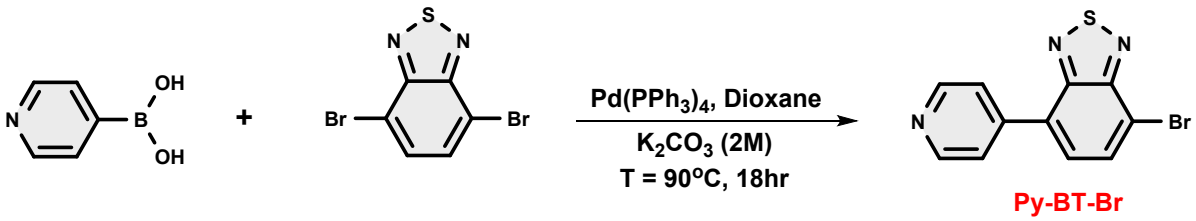
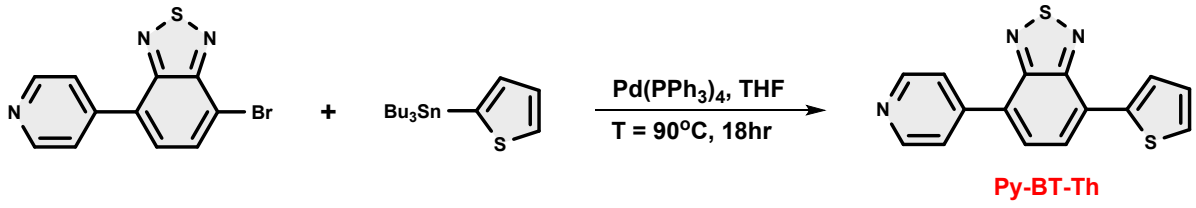
Instrumentation

A Bruker 400 MHz instrument is used to record the ^{1}H-NMR spectra of the catalyst in deuterated chloroform ($CDCl_3$) solvent. An Agilent 6545 Q-TOF LC−MS spectrometer was used to record the high-resolution mass spectra (HRMS) in acetonitrile solvent using the electron spray ionization (ESI) method. Absorption spectra were recorded at a 2nm data interval in a Perkin Elmer LAMBDA 1050+ UV/Vis/NIR spectrophotometer. The Fluorolog-3 and Horiba Delta Flex 01 instruments recorded the photoluminescence spectra and decay profile, respectively. A Bruker A300-9.5/12/S/W instrument was used to record the EPR/ESR spectra using the UV-visible 100 W Hg lamp at room temperature. Cyclic voltammetry experiments were performed on a CHI1200B electrochemical workstation, using an Ag/AgCl reference electrode, platinum wire counter electrode, and glassy carbon (GC) as the working electrode, using $[^{n}Bu_4N]^{+}[PF_6]^{-}$ as an electrolyte in acetonitrile solvent. The Newport power meter model 843-R was used to record the intensity of the light irradiation source.

Scheme for Py-BT-Th Synthesis



Scheme S1. Synthesis of Py-BT-Br by Suzuki-Miyaura coupling reaction.



Scheme S2. Synthesis of Py-BT-Th by Stille coupling reaction.

H_2O_2 Detection and Calibration Plot

After the reaction, extracted 2 mL aqueous phase was mixed with 0.5 mL of 0.1 M potassium hydrogen phthalate ($C_8H_5KO_4$) and 0.5 mL of 0.4 M potassium iodide (KI) solution, and then placed in the dark for 2 hours. The H_2O_2 molecules in the solution react with the I^- to generate I_3^-, which exhibits a characteristic absorption peak at 352 nm in the UV-visible spectrum. To quantify the H_2O_2 concentration, a calibration curve was made using the diluted standard 30% (w/v) H_2O_2 solution. Fig. S1 shows the calibration curve obtained by plotting the I_3^- absorbance at 352 nm as a function of H_2O_2 concentration and the corresponding UV-visible spectrum of

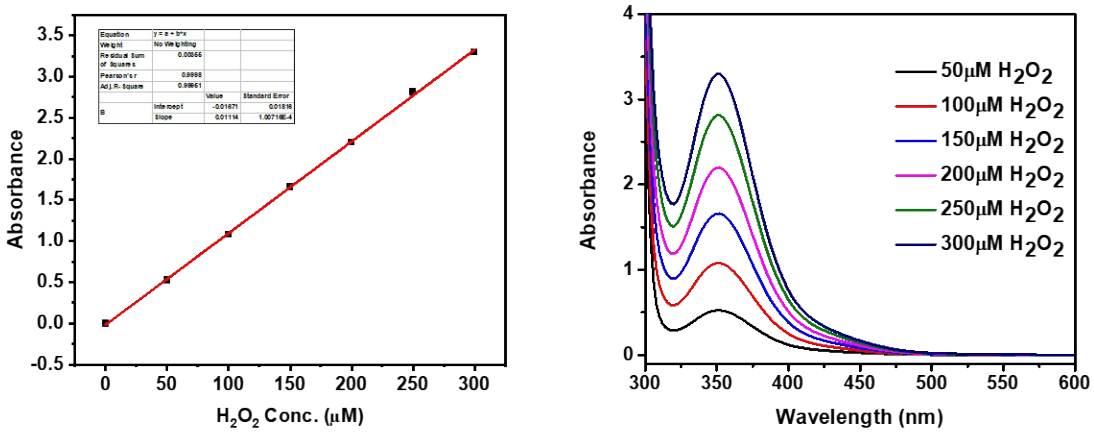


Fig. S1. (a) Calibration plot for H_2O_2 concentration vs. I_3^- absorbance at 352nm. (b) UV-visible absorption spectra of I_3^- at various H_2O_2 concentration.

known H_2O_2 concentration.

Turnover Frequency (TOF) Calculations

Turnover frequency (TOF) for the H_2O_2 production is calculated by using the following formula:

TOF = moles of H_2O_2 produced / (moles of catalysed utilised * time taken for reaction)

Moles of H_2O_2 produced = 214.36 mmoles

Time = 2 hours

Py-BT-Th Catalyst used = 1 g

Moles of Py-BT-Th = 1g / 295.38 g mol^{-1} = 3.385 mmoles

TOF = 214.36 mmoles of H_2O_2 produced / (3.385 mmoles of catalyst * 2 hour)

TOF = 31.66 h^{-1}

TOF = ~ 32 h^{-1}

Digital Photograph of Reaction Setup

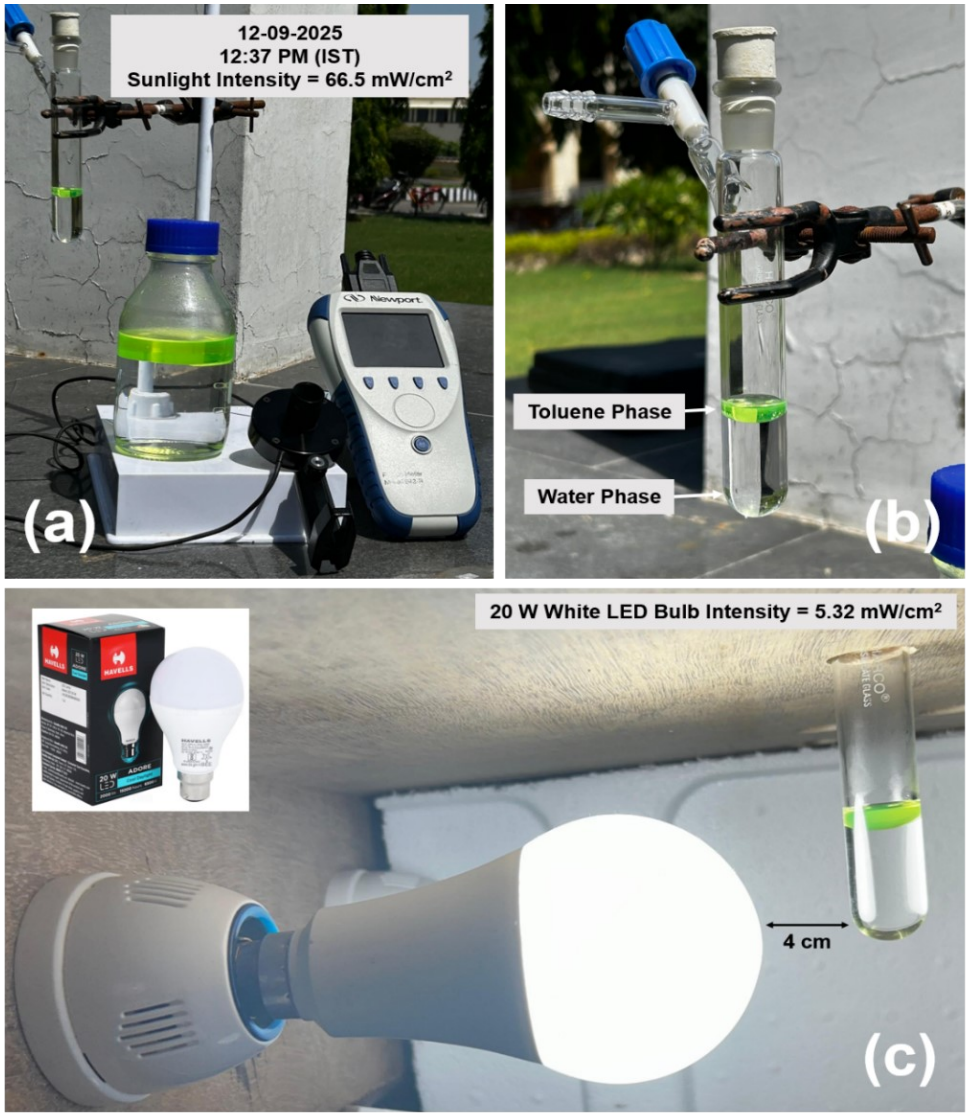


Fig. S2. (a) Digital photograph of photocatalytic H_2O_2 synthesis under natural sunlight with Newport 843-R power meter for intensity measurement. (b) Toluene-water two-phase system under natural sunlight for H_2O_2 production digital image. (c) Photocatalytic setup for H_2O_2 production using a 20 W white LED Bulb.

Biphasic *vs* Monophasic H_2O_2 synthesis

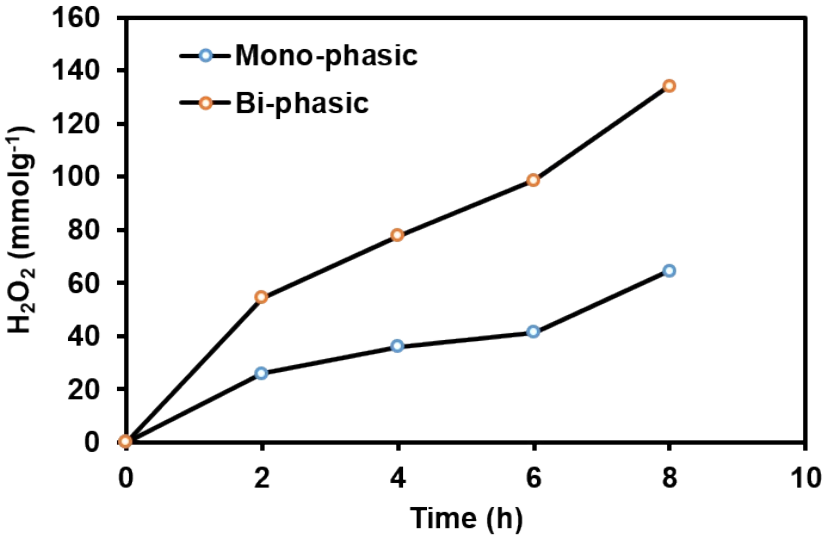


Fig. S3. H_2O_2 production in mono vs biphasic system. Monophasic reaction condition: Toluene 2mL, 100 µg catalyst, 10 µL TEA, 2 hours, 20 W white LED bulb, under ambient conditions with stirring. Biphasic reaction condition: Toluene: Water 2 mL:8mL, 100 µg catalyst, 10 µL TEA, 2 hours, 20 W white LED bulb, under ambient conditions with stirring.

Reusability Test Procedure

In a 15 mL Schlenk tube, 8 mL of deionized water is added, followed by 2mL toluene containing 100 µg photocatalyst and 10 µL triethylamine (TEA) without any mechanical stirring under an air atmosphere. Toluene and water resulted in a two-phase system, and the organic phase includes both the sacrificial donor and the catalyst. After that, the reaction solution is irradiated for 2 hours using a 20 W White LED Bulb at room temperature. Upon completion of the first catalytic cycle, the aqueous phase is completely extracted for the H_2O_2 quantification using the iodometry method, and the remaining organic layer, which consists of the catalyst, is again subjected to a new catalytic cycle by adding 8 mL deionized water and 10 µL of TEA and irradiated for 2 hours using a 20 W White LED Bulb. This exact procedure is

repeated up to five times to check the reusability of the photocatalyst Py-BT-Th. The catalyst exhibited moderately good reusability with an 18% reduction in activity in five consecutive cycles compared to the fresh catalytic cycle.

Scale up and Recyclability of the Catalyst Py-BT-Th

In a 500 mL transparent reagent bottle, 320 mL of deionized water is added, followed by the addition of 80 mL toluene containing 4000 µg Py-BT-Th photocatalyst and 400 µL triethylamine (TEA), and 5 minutes of oxygen bubbling. Toluene and water resulted in a two-phase system, and the organic phase includes both the sacrificial donor and the photocatalyst Py-BT-Th. After that, the reaction solution is irradiated for 2 hours under natural sunlight, under mechanical stirring. After 2 hours, the organic and aqueous phase is separated using a separating funnel. After that, 2 mL of the aqueous phase is subjected to the H_2O_2 quantification using the iodometry method. The extracted organic phase, consisting of the catalyst, is subjected to rotatory evaporation to recover the toluene and the photocatalyst Py-BT-Th. The recovered Py-BT-Th catalyst is then subjected to the ^1H NMR experiment to check the structural integrity of Py-BT-Th after photocatalysis. ^1H NMR experiment confirmed that the integrity of the photocatalyst Py-BT-Th structural core is retained after 2 hours of photocatalysis, showing that the catalyst is stable even after 2 hours of photocatalytic activity.

Long-term Photocatalytic Activity and Recyclability

In a 15 mL Schlenk tube, 8 mL of deionized water is added, followed by 2mL toluene containing 100 µg photocatalyst and 20 µL triethylamine under an oxygen atmosphere without any mechanical stirring. Toluene and water resulted in a two-phase system, and the organic phase includes both the sacrificial donor and the catalyst. After that, the reaction solution is irradiated for different time intervals using a 20 W White LED Bulb to check the long-term activity of the catalyst at room temperature. Upon completion of the reaction time, 2 mL of the aqueous phase is extracted for the H_2O_2 quantification using the iodometry method (shown in Fig. S3a. We then recovered the catalyst and performed photoluminescence and UV-visible spectroscopy to confirm its stability after 12 hours of long-term activity. We find that there is no change in the spectra before and after long-term activity, which confirms that the catalyst remains stable (see Fig. S4b & S4c and S4d & S4e).

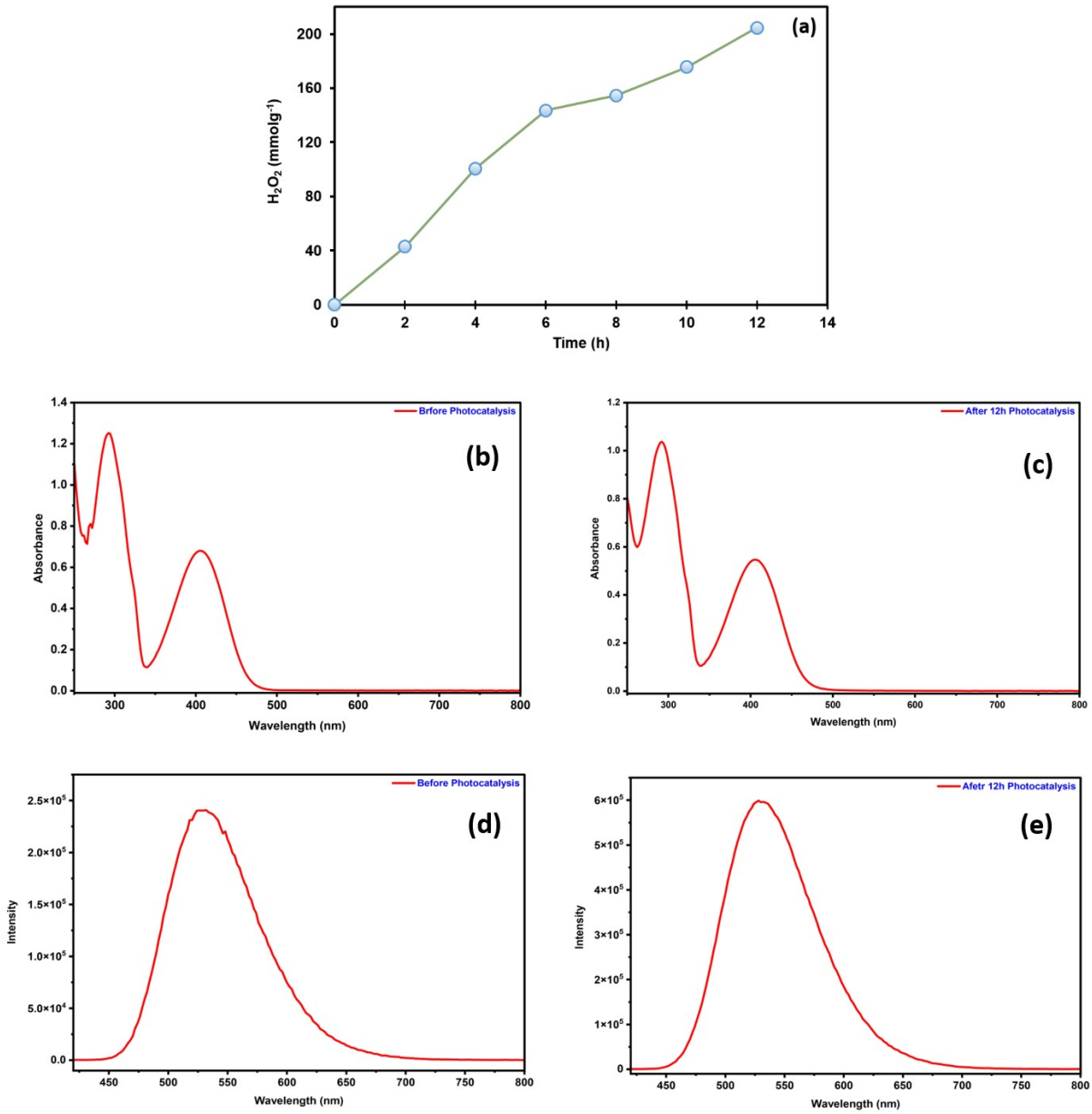


Fig. S4. (a) Upto 12 hours' long-term photocatalytic activity of Py-BT-Th catalyst. (b & c) UV-visible spectra before and after long-term photocatalytic activity in acetonitrile solvent. (c & d) Photoluminescence spectra before and after 12 hours' long-term activity in acetonitrile solvent.

PL, UV-Visible spectra, Lippert Matage & Stern-Volmer plot of Py-BT-Th

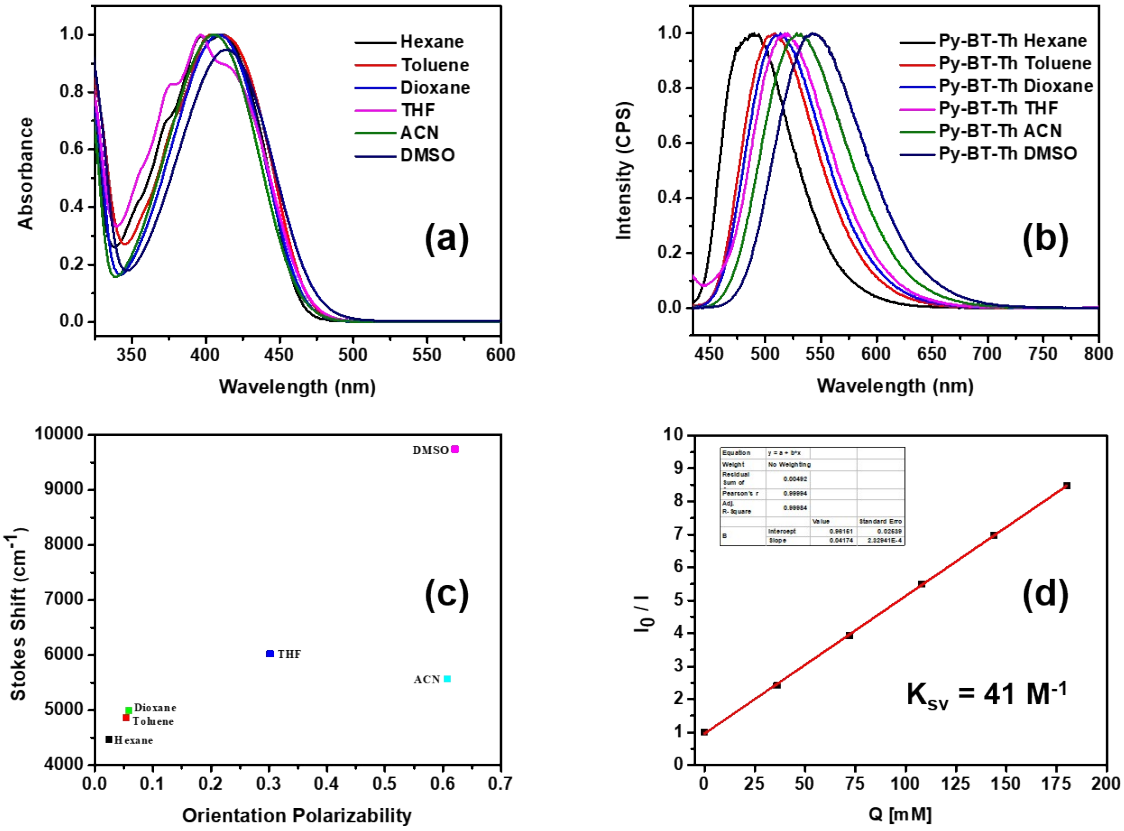


Fig. S5. (a) UV-visible absorption spectra of Py-BT-Th in different solvents. (b) PL spectra of Py-BT-Th in different solvents. (c) Lippert-Matage plot of Py-BT-Th. (d) Stern-Volmer plot of Py-BT-Th at λ_{em} = 530 nm in acetonitrile solvent with triethylamine as quencher obtained with linear fitting.

Cyclic Voltammogram

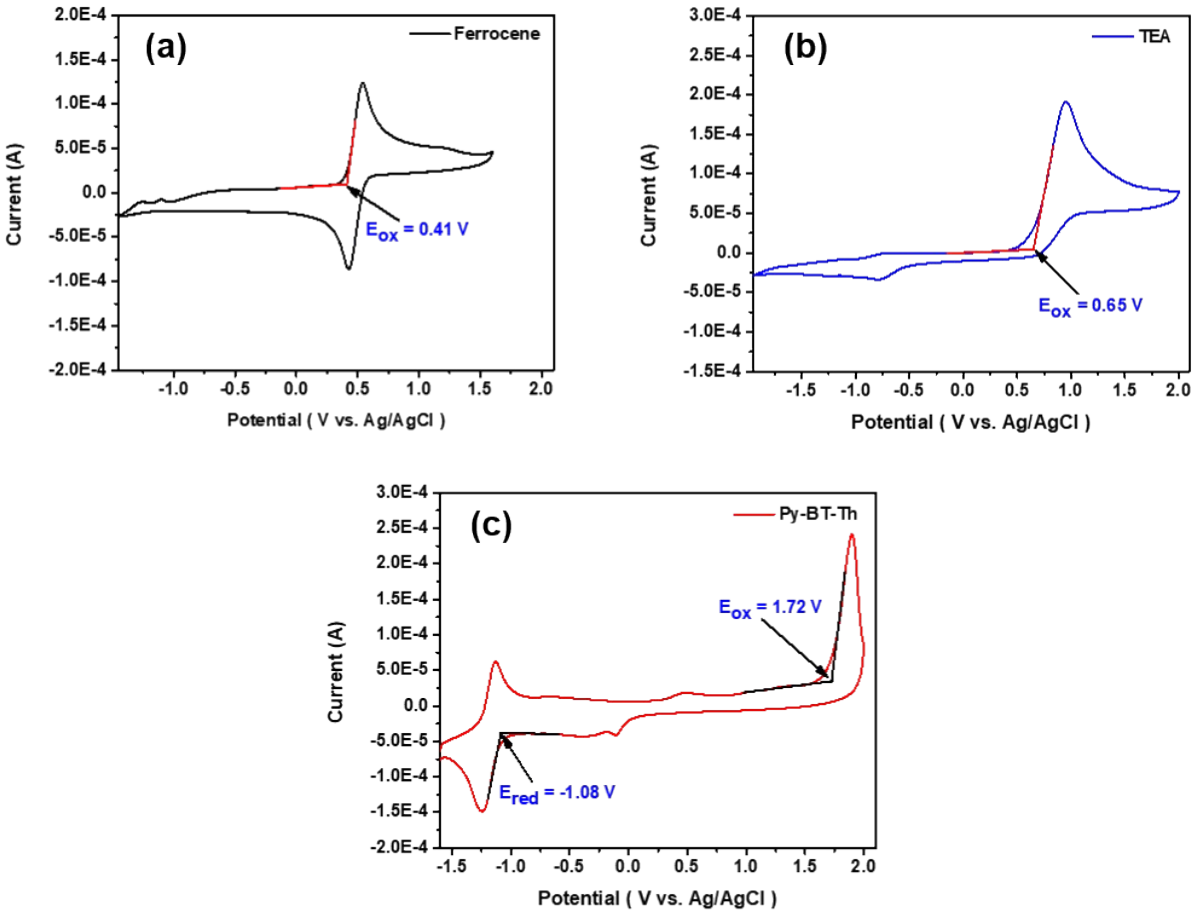


Fig. S6. Cyclic voltammogram of (a) ferrocene, (b) triethylamine (TEA), (c) Py-BT-Th catalyst in acetonitrile solvent under nitrogen atmosphere. Scan Rate = 0.1 V/s, Sample interval = 0.001 V, Sensitivity = $1e^{-4}$ A/V.

$E_{NHE} = E_{AgCl} + 0.197$, $E^{o}_{Ag/AgCl} = 0.197$ V vs NHE.

^{1}H and ^{13}C NMR Spectra of the Py-BT-Br and Py-BT-Th

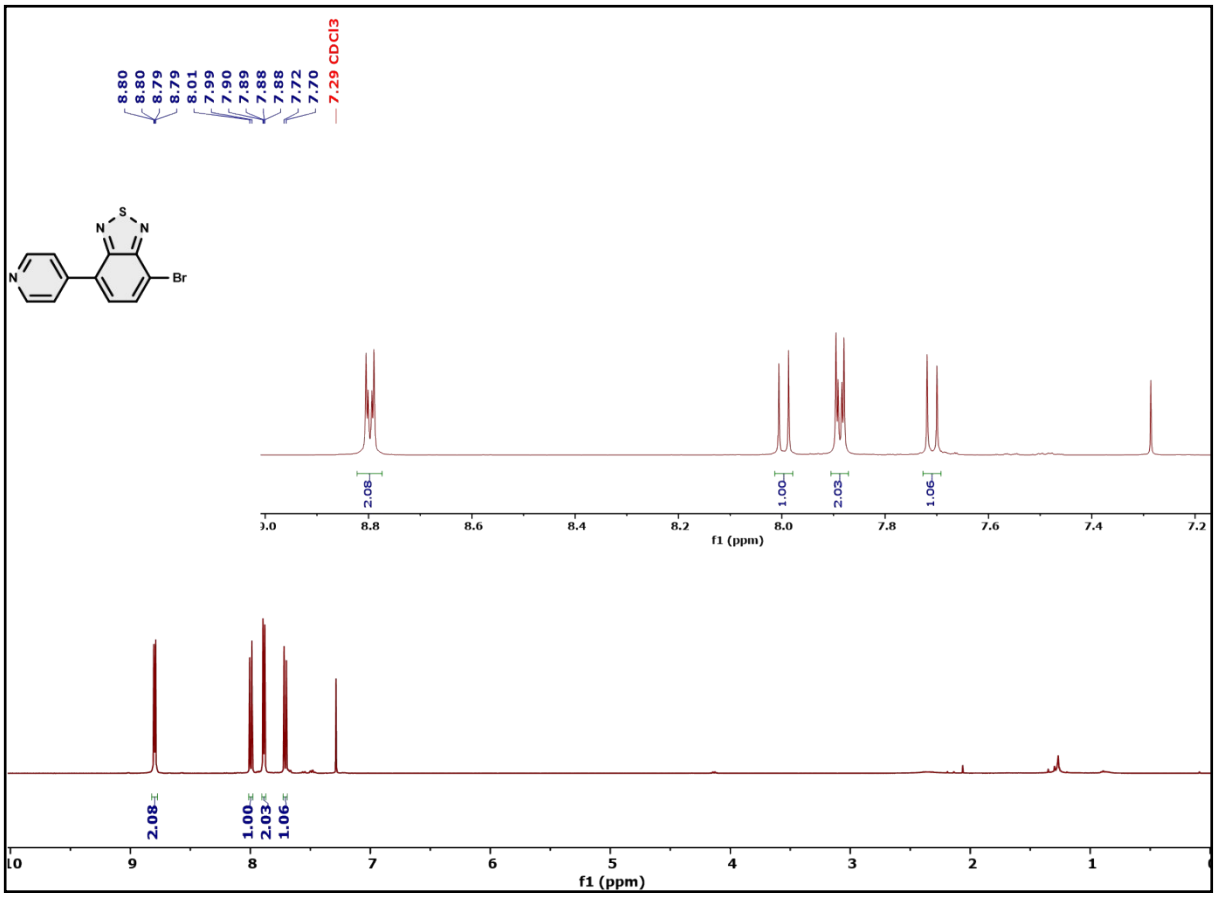


Fig. S7. ^{1}H NMR of Py-BT-Br.

^{1}H NMR (400 MHz, $CDCl_3$)

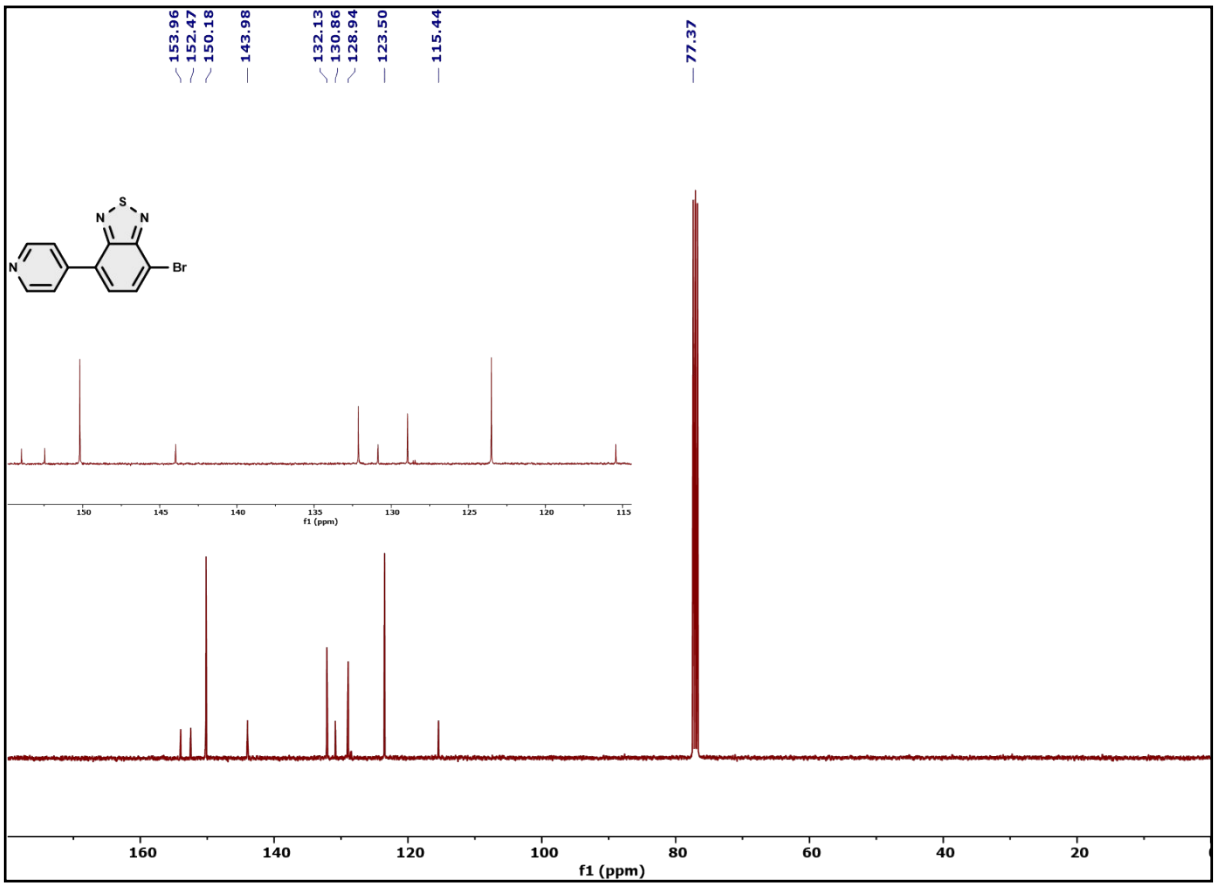


Fig. S8. ^{13}C NMR of Py-BT-Br.

^{13}C NMR (101 MHz, $CDCl_3$)

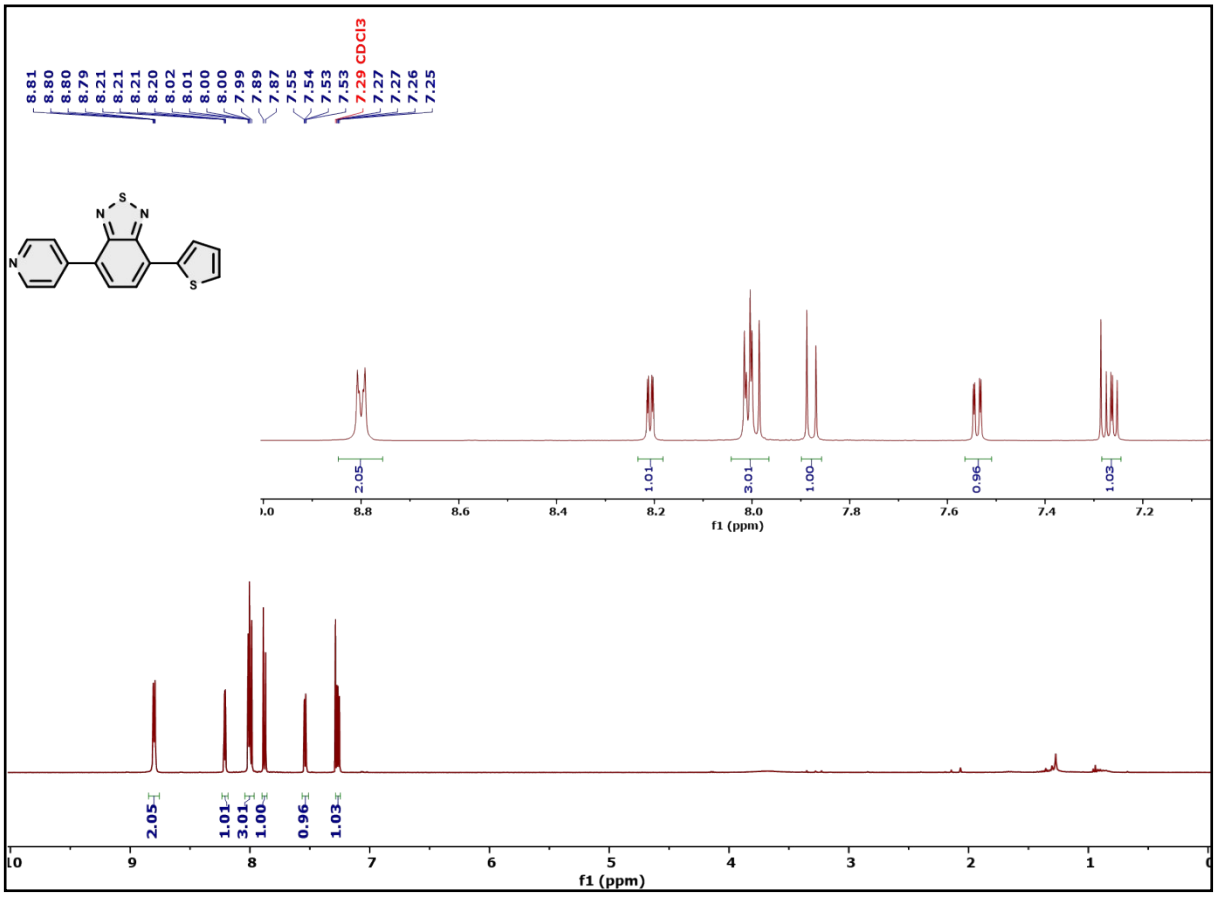


Fig. S9. ^{1}H NMR of Py-BT-Th.

^{1}H NMR (400 MHz, $CDCl_3$)

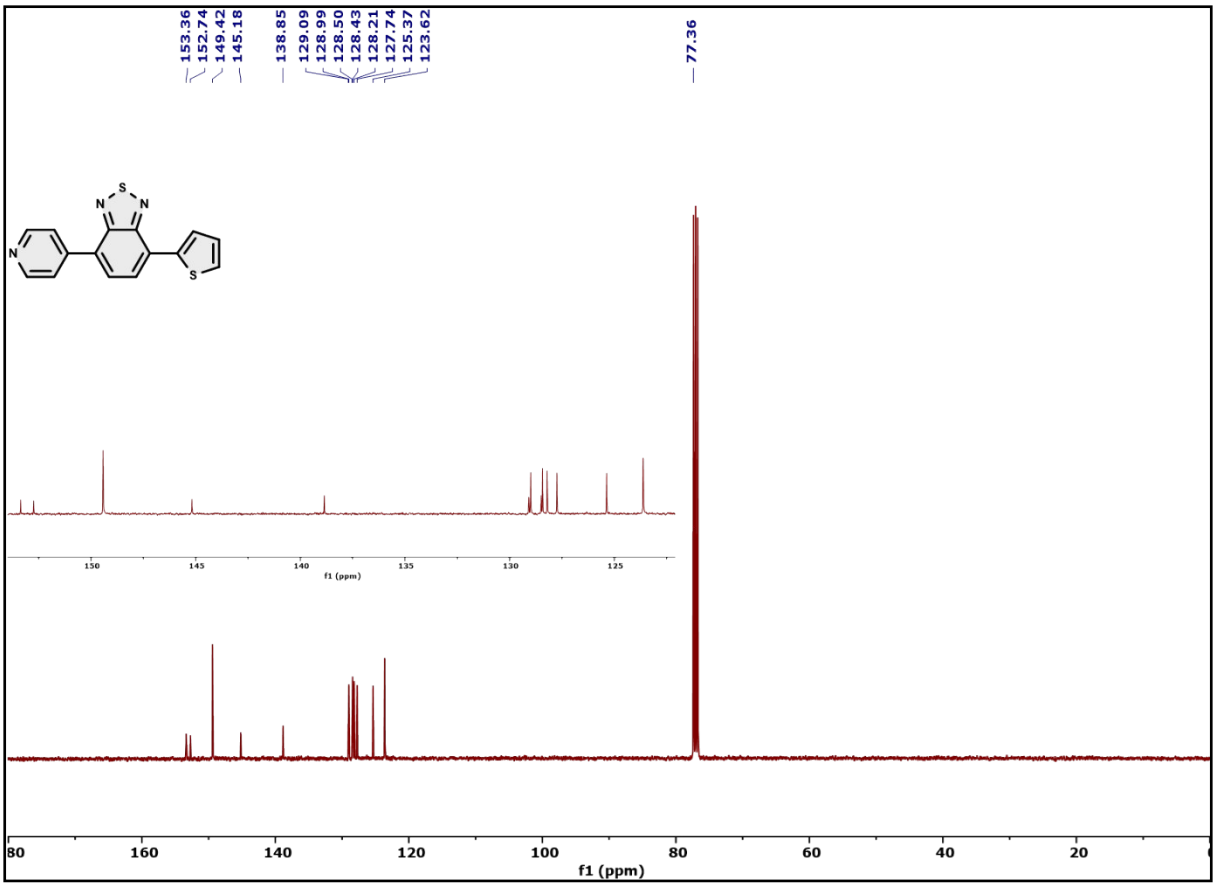


Fig. S10. ^{13}C NMR of Py-BT-Th.

^{13}C NMR (101 MHz, $CDCl_3$)

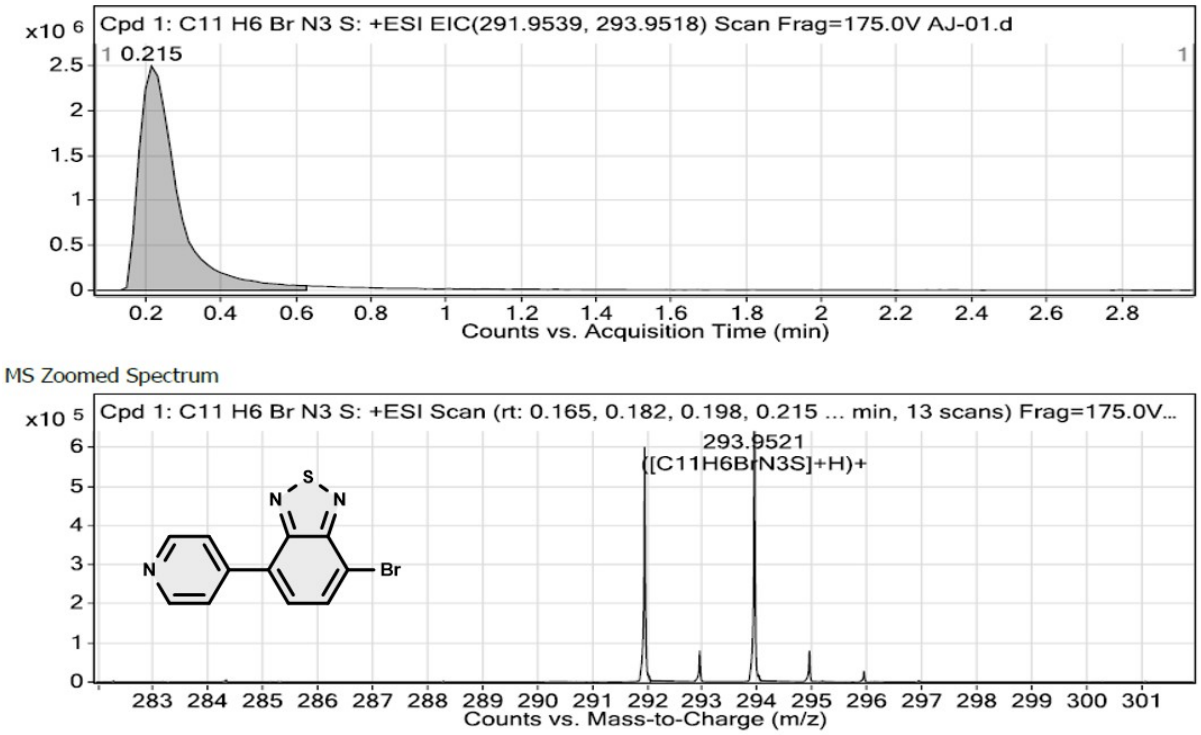


Fig. S11. HRMS spectra of Py-BT-Br.

HRMS Data of Py-BT-Br and Py-BT-Th

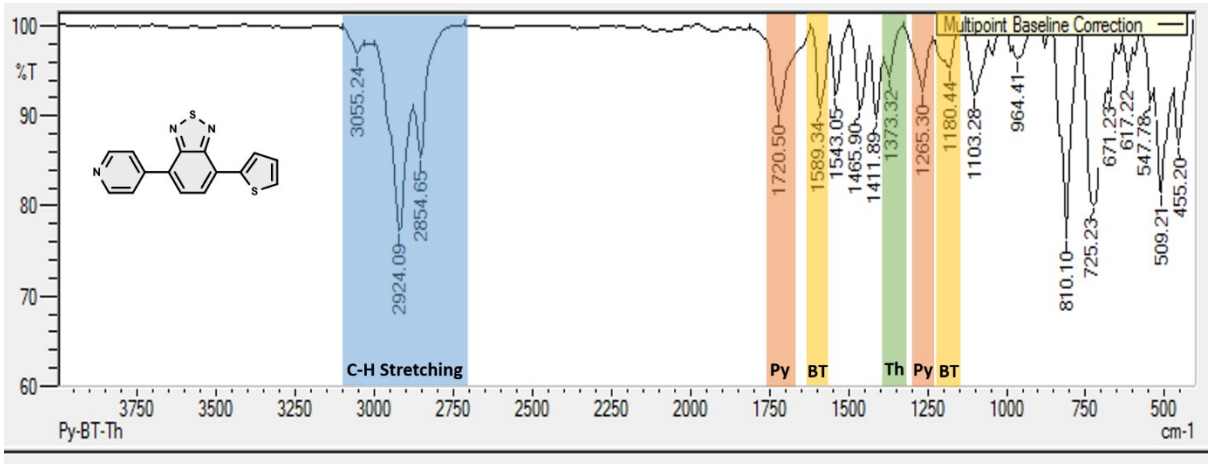


Fig. S13. FTIR spectra of catalyst Py-BT-Th.

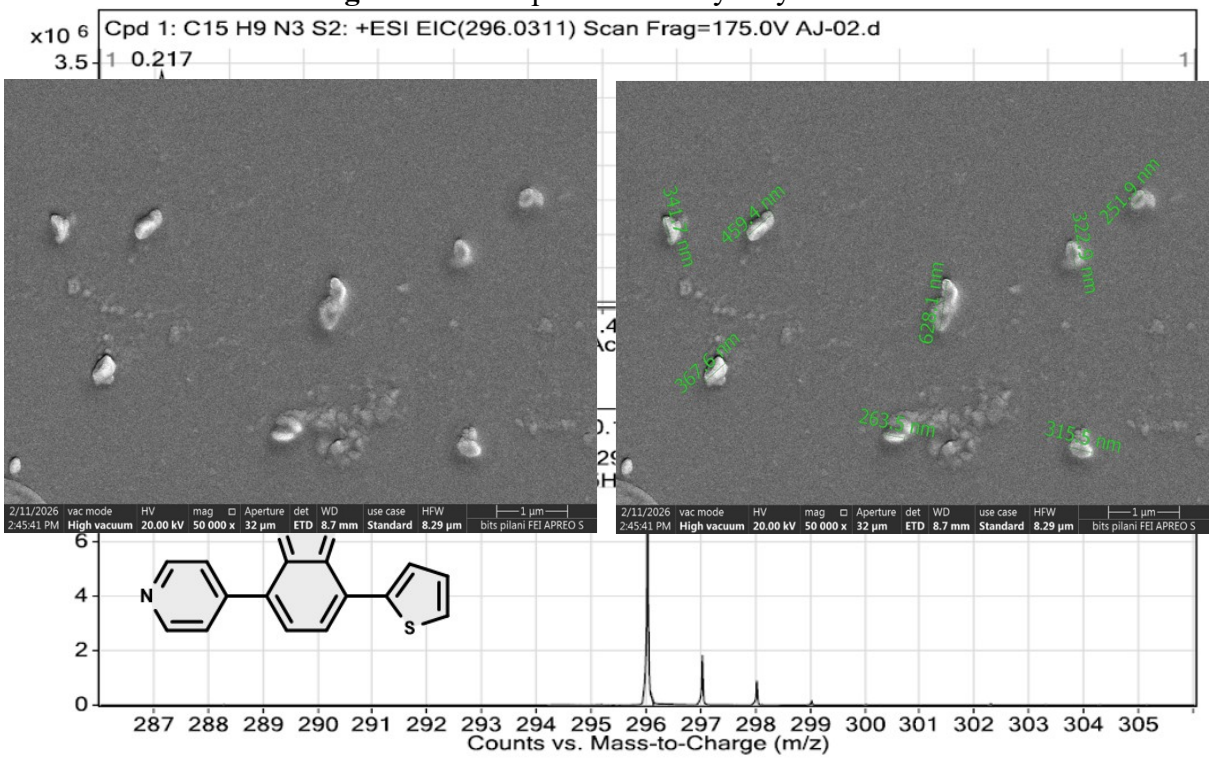


Fig. S12. HRMS spectra of Py-BT-Th.

Fig. S14. SEM image of Py-BT-Th.

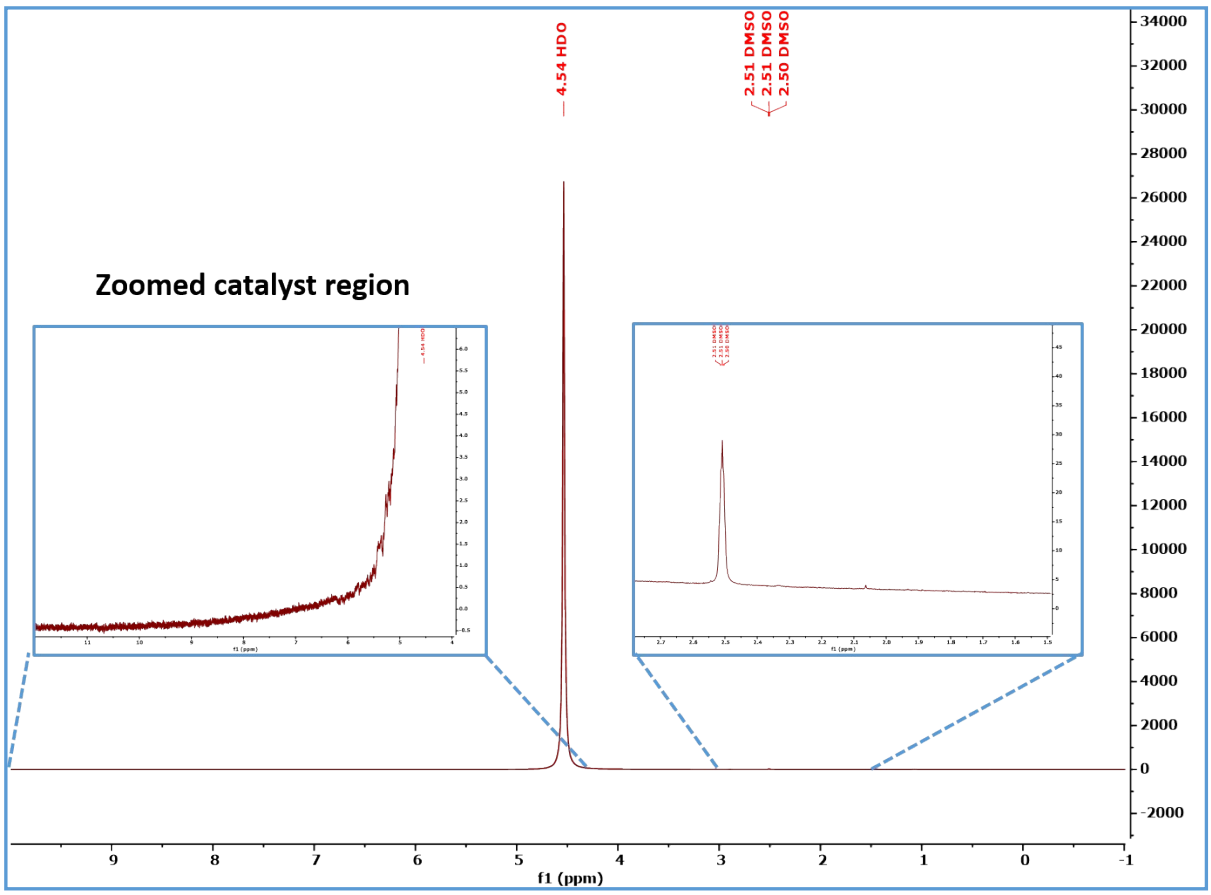


Fig. S15. ^{1}H NMR spectra of aqueous layer after the photocatalytic H_2O_2 synthesis.

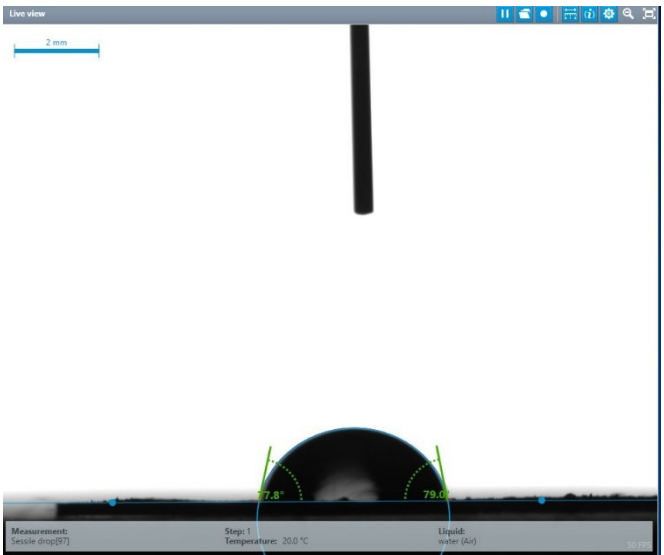


Fig. S16. Water contact angle of Py-BT-Th catalyst.

Comparison of Photocatalytic H_2O_2 Production Rate with the Reported Literature

Table S1. Comparison of the H_2O_2 production rate of Py-BT-Th with the benzothiadiazole-based reported photocatalytic system.

S.No.	Catalyst	Solvent System Light Source	H_2O_2 Production Rate ($mmolg^{-1}h^{-1}$)	Reference
1	TAPT-BT-COF	H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	1.36	Catal. Sci. Technol., 2023, 13, 6463-6471
2	TTF-BT-COF	H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	2.76	Angew. Chem., Int. Ed. 2023, 62 (9), e202218868
3	H2Se-COF	H_2O: BA 300 W Xenon lamp ($\lambda > 420$ nm)	6.1	Angew. Chem. Int. Ed. 2024, 63, e202405313
4	Hz-TP-BT-COF	H_2O Xenon Lamp Full Spectrum H_2O Natural Sunlight	12.7 2.7	Nat. Catal. 2024, 7 (2), 195−206
5	JUC-675	CH_3CN-BA 300 W Xenon lamp ($\lambda > 420$ nm)	22.7	Angew. Chem. Int. Ed. 2025, 64, e202416240
6	COF-BCTB BT	Water: THIQ 300 W Xenon lamp ($\lambda > 420$ nm)	82.6	J. Am. Chem. Soc. 2025, 147, 24, 20855–20864
7	**Py-BT-Ph***	**H_2O: Toluene + TEA** **20 W White LED Bulb** **Intensity 5.32 mW/cm²**	**61.51**	**This work**
8	**Py-BT-Ph***	**H_2O: Toluene + TEA** **Natural Sunlight** **Intensity 66.5 mW/cm²**	**107.18**	**This work**

Reaction Condition: 100 µg Py-BT-Th catalyst, 10 µL TEA, Toluene: Water (2 mL:8 mL), 2-hour reaction time.

(* indicates homogeneous recyclable two-phase system)

Table S2. Comparison of the photocatalytic H_2O_2 production rate of Py-BT-Th with various reported photocatalytic materials.

S.No.	Catalyst	Solvent System	H_2O_2 Production Rate ($mmolg^{-1}h^{-1}$)	Reference
1	PAF-363	H_2O: EtOH 300 W Xenon lamp ($\lambda > 420$ nm)	11.7	Angew. Chem. Int. Ed. 2024, 63, e202402095
2	TFPA-TAPT COF-Q	H_2O:BA 300 W Xenon lamp	11.8	Nat. Commun. 2024, 15, 1267
3	PD^{2+} COF167	H_2O: EtOH 300 W Xenon lamp ($\lambda > 400$ nm)	11.9	Angew. Chem. Int. Ed. 2023, 62, e202315456
4	JNM-25	H_2O: IPA 300 W Xenon lamp	17.4	Angew. Chem. Int. Ed. 2024, 63, e202408186
5	CTF-BTT	H_2O: BA 300 W Xenon lamp ($\lambda > 420$ nm)	74.9	Angew. Chem. Int. Ed. 2025, 64, e202416350
6	Re10-MFM-67	BzOH/H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	8.5	J. Am. Chem. Soc. 2025, 147, 28, 24326–24335
7	SonoCOF-F2	BzOH/H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	2.74	J. Am. Chem. Soc. 2022, 144, 9902-9909
8	PTH-SO2-COF	MeOH/H_2O 300 W Xenon lamp	13.57	Angew. Chem., Int. Ed. 2025, 64, e202423055
9	TP-PCN	Isopropanol/H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	6.53	Angew. Chem., Int. Ed. 2021, 60, 25546-25550
10	ASCN	ACN/H_2O/4-MeO-BA 300 W Xenon lamp AM 1.5G	8.07	J. Am. Chem. Soc. 2023, 145, 20837-20848
11	PCN-NaCA	Glycerol aqueous solution Solar simulator	18.70	Nat Commun. 2021, 12, 3701
12	O/K-CN	Isopropanol/H_2O 300 W Xenon lamp ($\lambda > 420$ nm)	15.47	Adv. Funct. Mater. 2022, 32, 2205119
13	**Py-BT-Ph***	**H_2O: Toluene + TEA** **20 W White LED Bulb** **Intensity 5.32 mW/cm^2**	**61.51**	**This work**

14	**Py-BT-Ph***	**H_2O: Toluene + TEA** **Natural Sunlight** **Intensity 66.5 mW/cm^2**	**107.18**	**This work**

Reaction Condition: 100 µg Py-BT-Th catalyst, 10 µL TEA, Toluene: Water (2 mL:8 mL), 2-hour reaction time.

(* indicates homogeneous recyclable two-phase system)