Supporting Information

Using Newly Designed Porphyrin Photocatalyst Based on Triptycene to Emulate Natural Photosynthesis for Regioselective Fixation of $NAD(P)^+$ to NAD(P)H and Synthesis of Value-Added Chemicals

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1. Instruments and Measurements:

UV-Visible spectroscopy was recorded on Shimadzu UV-1900i spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using Shimadzu 8000 IRspirit spectrometer using the KBr pellet support. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer using Cu Kα radiation (λ=1.5418Å), 40kV, 40mA). Scanning electron microscope (SEM) images and elemental mapping were obtained on a Tescan Mira 3 LMU FEG SEM, Accelerating voltage: 10 kV, Coating: Quorum Q150T ES / 20 mA 60sec Pt coating. X-ray photoelectron spectroscopy (XPS) spectra were recorded on British Kratos's AXIS SUPRA (monochromatic Al-Kα (1486.7eV). Cyclic Voltammetry, Tafel plot, EIS were performed on CHI608E, 220V instrument. Raman spectra obtained on Rigaku Mini Flex benchtop and LabRam HR with 532 nm laser excitation. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL RESONANCE ECZ500R operating at 500 MHz (Tetramethylsilane (TMS), as internal standards). ^{1}H NMR spectra of monomer P (Fig. S13) was recorded on a Bruker AVANCE II + 300 MHz spectrometer with TMS reference standard.

2. Materials and Methods

Boron trifluoride diethyl etherate, 4-bromobenzaldehyde, DCM, p-chloranil, triptycene, $AlCl_3$, nicotinamide adenine dinucleotide (NAD^+), nicotinamide adenine dinucleotide phosphate ($NADP^+$), ascorbic acid, sodium phosphate monobasic dihydrate (NaH_2PO_4. $2H_2O$), sodium phosphate dibasic di-hydrate ($Na_2HPO_4.2H_2O$), 2,2'-bipyridine, N,N-dimethylformamide, were purchased from Sigma Aldrich. Benzaldehyde, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, ethanol, methylacetoacetate, methanol, acetone, and DMF were purchased from TCI chemicals. Organometallic electron mediator (EM), [Cp*Rh(bpy)Cl]Cl, (Cp* = pentamethylcyclopentadienyl, bpy = 2,2′-bipyridyl) was synthesized as descriptive in previous literature[1]. Deionized water was obtained using a double distillation.

3. Synthesis of tetrabromophenyl-porphyrin (P)

A porphyrin derivative was synthesized in a two-necked round-bottom flask by combining 1 mL of pyrrole, 1 g of 4-bromobenzaldehyde, and 100 mL of DCM. Boron trifluoride diethyl etherate ($BF_3.OEt_2$) was slowly added to the reaction mixture, which was then stirred at room temperature in the dark for 3 hours. Subsequently, 1.85 g of p-chloranil was added, and the reaction mixture was refluxed for 1 hour. Upon cooling, the reaction mixture was filtered and rinsed thoroughly with DCM. The filtrate was concentrated under reduced pressure using a rotary evaporator, yielding the desired porphyrin product 40 % (399 mg), which was stored for future use. Synthesis of monomer P characterized by ^{1}H-NMR ($CDCl_3$): δH -2.88 (s, 2H, H_{NH}), 7.89 (d, 8H, H_{phenyl}), 8.05 (d, 3J=8.2 Hz, 8H, H_{phenyl}), 8.83 (s, 8H, $H_{pyrrole}$).[2,3]

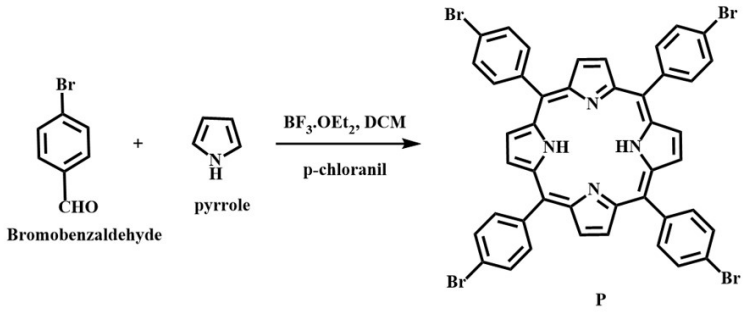


Fig. S1. Synthesis of monomer tetrabromophenyl-porphyrin (P).

3. **Synthesis of PBT photocatalyst**

The PBT photocatalyst was synthesized by Friedel-Crafts alkylation of triptycene (T) with tetrabromophenyl porphyrin (P) as a cross linker promoted by Lewis acid $AlCl_3$. A mixture of T (130 mg, 1equivalent, 0.511mmol), P (356.6 mg, 0.75 equivalent, 0.383 mmol), and $AlCl_3$ (500 mg) was prepared in a 100 mL round-bottom flask and subsequently add 20 mL of dichloromethane. The resulting green solution was stirred under a nitrogen atmosphere for 24 hours, leading to the formation of a network-like precipitate. The resulting precipitate was washed three times with diluted HCl, CH_3OH, DCM and CH_3COCH_3, respectively, to remove catalyst and unreacted monomers. The product was purified through Soxhlet extractor in methanol for 24 h in order to remove all the remaining catalyst and monomer and finally dried under reduced pressure for 24 h. The PBT photocatalyst product obtained by 65% yield (316 mg). [4,5]

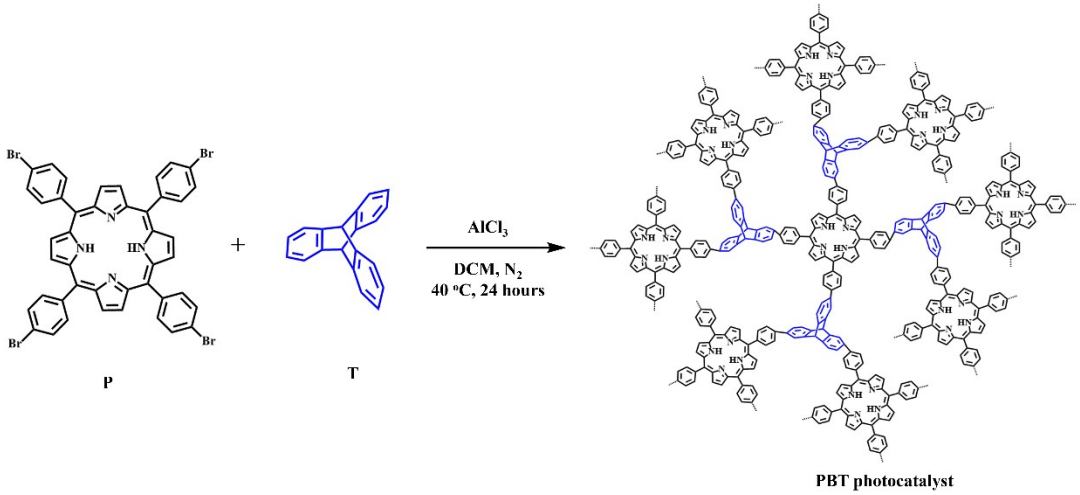


Fig. S2. Synthesis route of PBT photocatalyst.

4. UV-visible spectrum of P and T

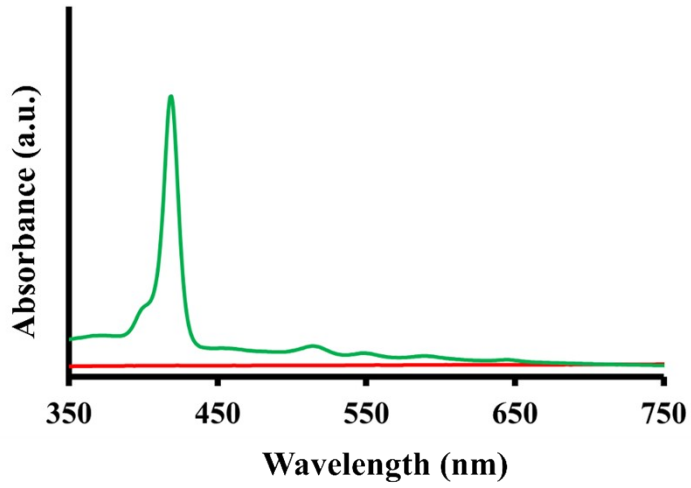


Fig. S3. UV-visible spectrum of P (green) and T (red).

5. XRD analysis

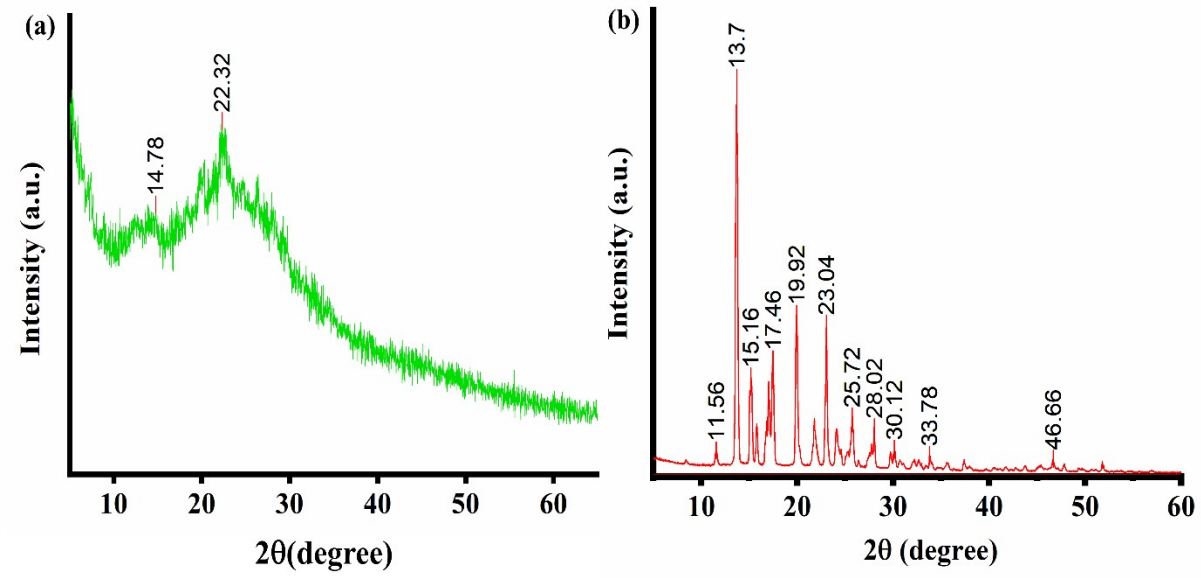


Fig. S4. X-ray diffraction pattern of P, and (b) T.

6. Calculations for HOMO and LUMO energy levels

The HOMO (E = - 5.70 eV) and LUMO (E = -3.35 eV) values of PBT were acquired from the following equation:

$E_{HOMO} = -(E_{ox} + 4.5) = -(1.08 + 4.5) = -5.70$ eV

$E_{LUMO} = -(E_{red} + 4.5) = -(-1.15 + 4.5) = -3.35$ eV

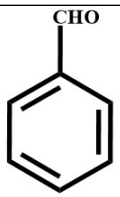
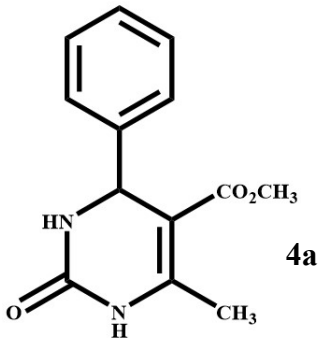
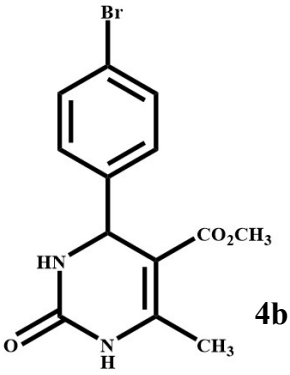
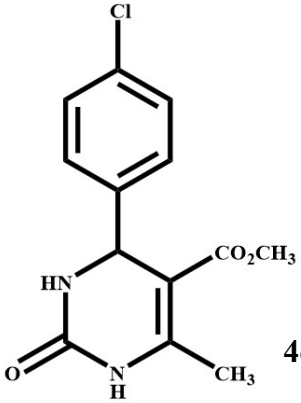
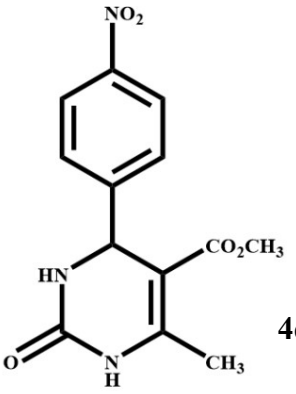
The E_{ox} and E_{red} values of PBT were obtained from CV measurements.

Table S1. Optimization of the reaction condition in the presence of different solvents.

Entry	Solvent	T (minutes)	(%) Yield
1.	**CH_3CN**	**30**	**72**
2.	**CH_3OH**	**5**	**70**
3.	**C_2H_5OH**	**5**	**97**
4.	**THF**	**5**	**30**
5.	**H_2O**	**5**	**85**
6.	**CH_2Cl_2**	**5**	**35**
7.	**$CH_3CO_2CH_3$**	**5**	**70**
8.	**DMF**	**5**	**40**
9.	**---**	**5**	**15**
10.	**DMSO**	**5**	**30**

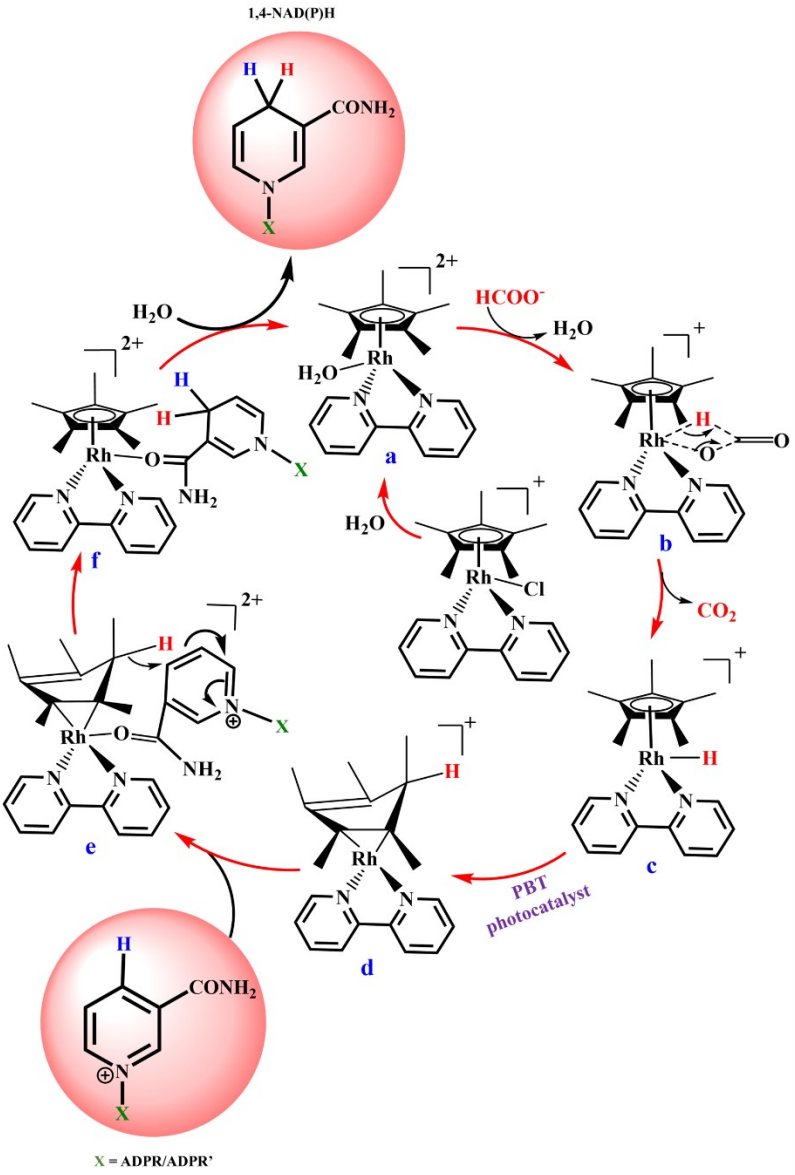
Reaction conditions. Aromatic aldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **1**), and PBT photocatalyst (5 mg) in various solvents were stir under room temperature conditions for appropriate time.

Table S2. Synthesis of value added chemical DPH derivatives via PBT photocatalyst.

Entry	Aldehyde	Product	Time (minute)	%Yield	Melting point
1.		 **4a**	**5**	**97**	**156-159**
2.		 **4b**	**5**	**95**	**177-179**
3.		 **4c**	**5**	**90**	**178-181**
4.		 **4d**	**5**	**94**	**211-214**

Reaction conditions. Aromatic aldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **1**), and PBT photocatalyst (5 mg) in various solvents were stir under room temperature conditions for 5 minutes.

7. Possible route for selective 1,4- NAD(P)H regeneration via PBT photocatalyst



Scheme S1. Schematic representation of mechanistic pathway for photogeneration of 1,4-NAD(P)H cofactor under solar light analogue with reduction of rhodium complex.

8. Quantum efficiency of PBT photocatalyst for NAD(P)H regeneration

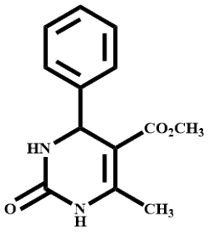
The concentration of NAD(P)H was spectrophotometrically measured through the change in absorbance of NAD(P)H at 340 nm in UV visible spectrum by using the absorption coefficient of 6220 M^{-1} cm^{-1}. The quantum efficiency was calculated using the given equation as under:

$$Quantum\ Efficiency\ (QE)\% = 2 \times \frac{Moles\ of\ NAD(P)H\ produced}{Moles\ of\ incident\ photons} \times 100$$

The QE was calculated to be 14.9 (14.1) % for the photocatalytic NAD(P)H regeneration process.[6]

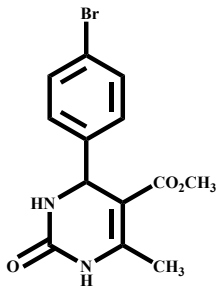
9. Spectroscopic data (^{1}H-NMR) of compounds 4a, 4b, 4c, 4d,

Synthesis of methyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a)



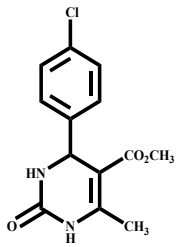
4a was synthesized as per the general procedure using benzaldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **3**) and Ethanol (3mL). A brown colour product obtained. The NMR data are in full agreement with those previously published in the literature.[7,8] **Yield: 97%** , M.p: 156-159; ^{1}HNMR (500 MHz, CD_3SOCD_3): 2.46 (3H, s, CH_3), 3.46 (3H, s, OCH_3), 5.38 (1H, s, H benzylic), 7.18 (2H, d, J= 7.2 Hz, HAr), 7.46 (2H, t, J=7.2 Hz, HAr), 7.73 (1H,s, J= 7.2Hz, Har), 7.90 and 9.20 (2H, 2s, 2NH). ^{13}C NMR (500 MHz, CD_3SOCD_3): δ 18.32 ($\underline{CH_3}$-CH=CH), 53.92 (Ar-$\underline{CH}$N), 59.80 (CO-$\underline{OCH_3}$), 99.32, 128.40 (CH_3-$\underline{CH}$=$\underline{CH}$), 127.83, 129.63,131.67, 132.0, 149.27,158.18 (CAr), 160.12 ($\underline{C}$=ONH), 165.73 (C=O ester).

Synthesis of methyl-4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b)



4b was prepared as per the general procedure using bromo benzaldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **3**) and Ethanol (3mL). A light-yellow product was obtained. **Yield: 95%;** Melting point. 202-204 °C; ^{1}HNMR (500MHz, CD_3SOCD_3) 2.30(3H, s, CH_3), 3.59 (3H, s, OCH_3), 5.14 (1H, s, $H_{benzylic}$), 7.56 (2H, d, J= 7.2 Hz, HAr), 8.13 (2H, d, J=7.2 Hz, HAr), 7.97 and 9.31 (2H, 2s, 2NH). ^{13}C NMR (500 MHz, CD_3SOCD_3): δ 18.36 ($\underline{CH_3}$-CH=CH), 51.34 (Ar-$\underline{CH}$N), 54.29 (CO-$\underline{OCH_3}$), 99.49, 126.69 (CH_3-$\underline{CH}$=$\underline{CH}$), 127.83,129.00, 129.68,129.79, 145.18, 149.22 (CAr), 152.70 ($\underline{C}$=ONH), 166.36 (C=O ester).

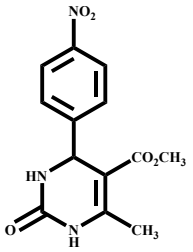
Synthesis of methyl-4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c)



4c was prepared as per the general procedure using chlorobenzaldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **3**), and Ethanol (3mL). A brownish yellow colour product obtained. The NMR data are in full agreement with those previously published in the literature. **Yield: 90%,** M.p:178-181; Yield: 90%; M.p:

177-179, 1HNMR (500MHz, CD_3SOCD_3) 2.46(3H, s, CH_3), 3.48 (3H, s, OCH_3), 5.39 (1H, s, H benzylic), 7.19 (2H, m, J= 7.2 Hz, HAr), 7.80 and 9.28 (2H, 2s, 2NH). ^{13}C NMR (500 MHz, CD_3SOCD_3): δ 17.74 ($\underline{CH_3}$-CH=CH), 51.66 (Ar-$\underline{CH}$N), 54.39 (CO-$\underline{OCH_3}$), 100.93, 126.83 (CH_3-$\underline{CH=CH}$), 129.10,129.17,129.78,133.40,143.79, 145.86 (CAr), 166.17 ($\underline{C}$=ONH), 167.88 (C=O ester)

Synthesis of methyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d)



4d prepared as per the general procedure using nitro benzaldehyde (1.0 mmol, **1**), urea (1.5 mmol, **2**), methyl acetoacetate (1.0 mmol, **3**), and Ethanol (3mL). Product 2c was obtained. **Yield: 94%;** M.p: 211-214, ^{1}HNMR (500 MHz, CD_3SOCD_3): 2.46(3H, s, CH_3), 3.52 (2H, s, OCH_3), 5.13 (1H, s, $H_{benzylic}$), 7.17-7.22 (2H, d, J= 7.2 Hz, HAr), 7.23-7.32 (2H, d, J=7.2 Hz, HAr), 7.91 and 9.64 (2H, 2s, 2NH). ^{13}C NMR (500 MHz, CD_3SOCD_3): δ 17.74 ($\underline{CH_3}$-CH=CH), 51.65 (Ar-$\underline{CH}$N), 54.40 (CO-$\underline{OCH_3}$), 100.93, 126.84 (CH_3-$\underline{CH=CH}$),128.25, 129.11, 129.17, 129.79,143.81, 145.87 (CAr), 166.16 ($\underline{C}$=ONH), 174.76 (C=O ester).

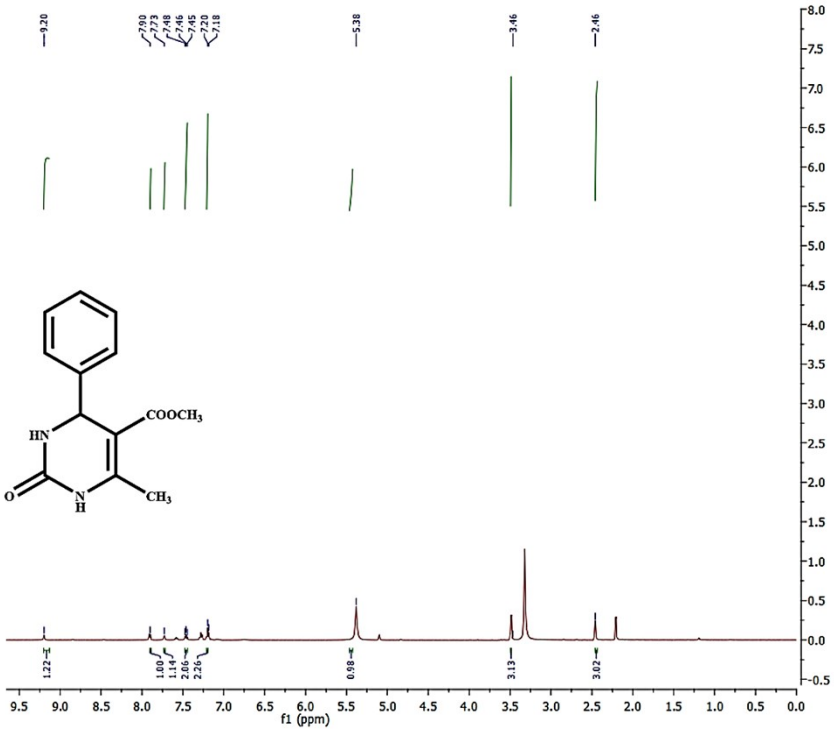


Fig. S5. ^{1}HNMR spectrum of the compound **4a**.

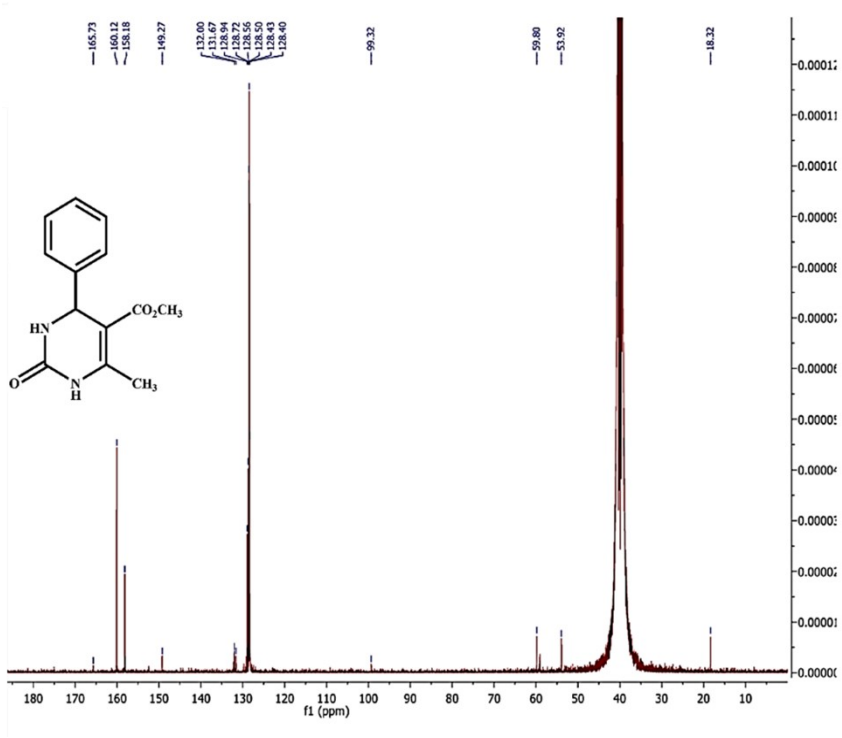


Fig. S6. ^{13}C-NMR spectrum of the compound **4a**.

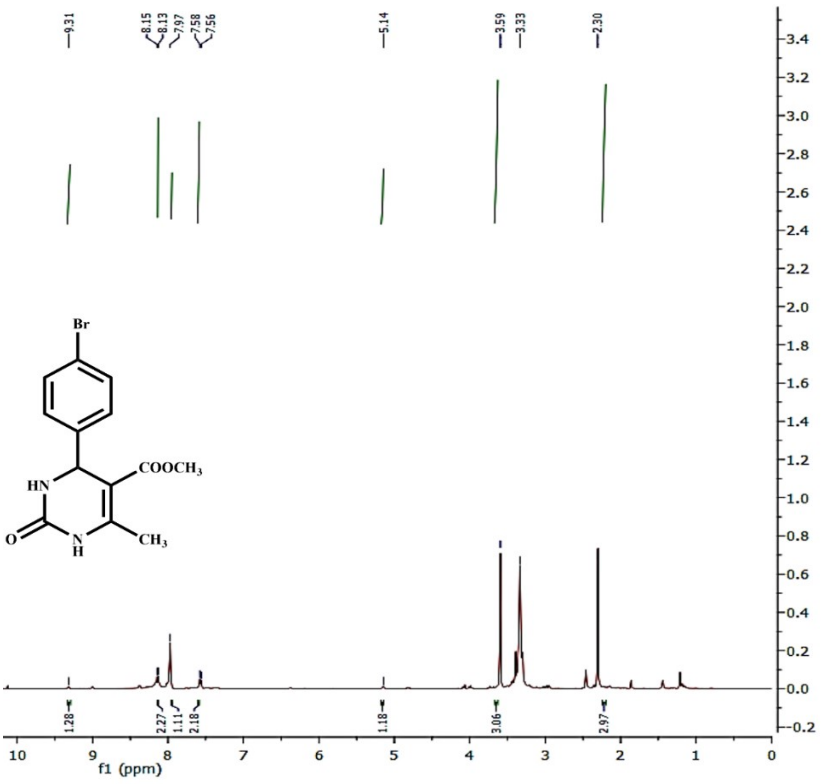


Fig. S7. ^{1}HNMR spectrum of the compound **4b**.

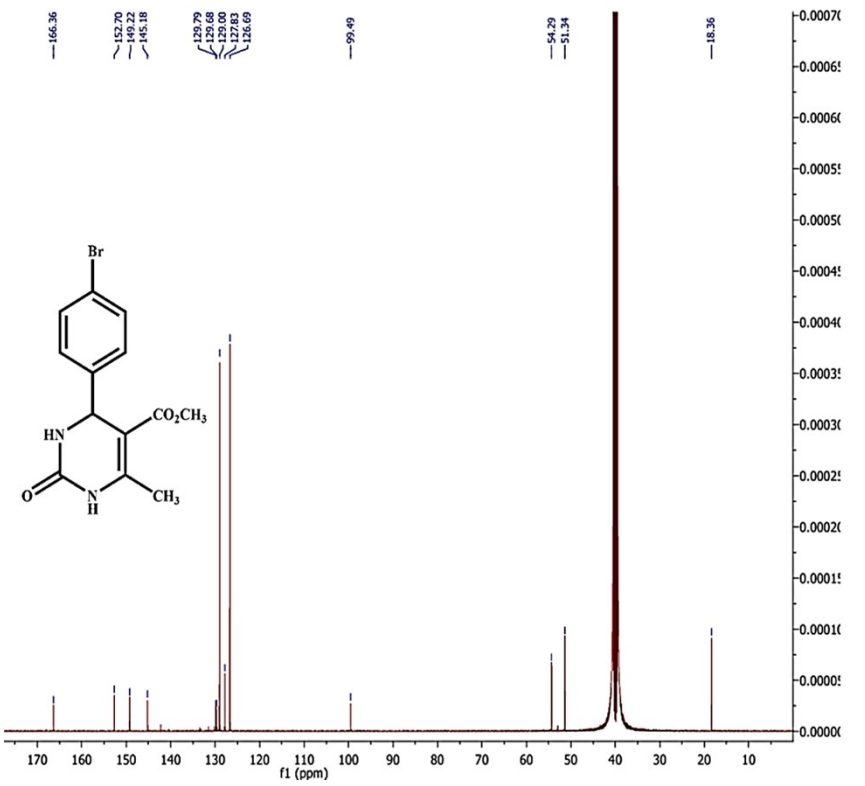


Fig. S8. ^{13}C-NMR spectra of compound **4c**.

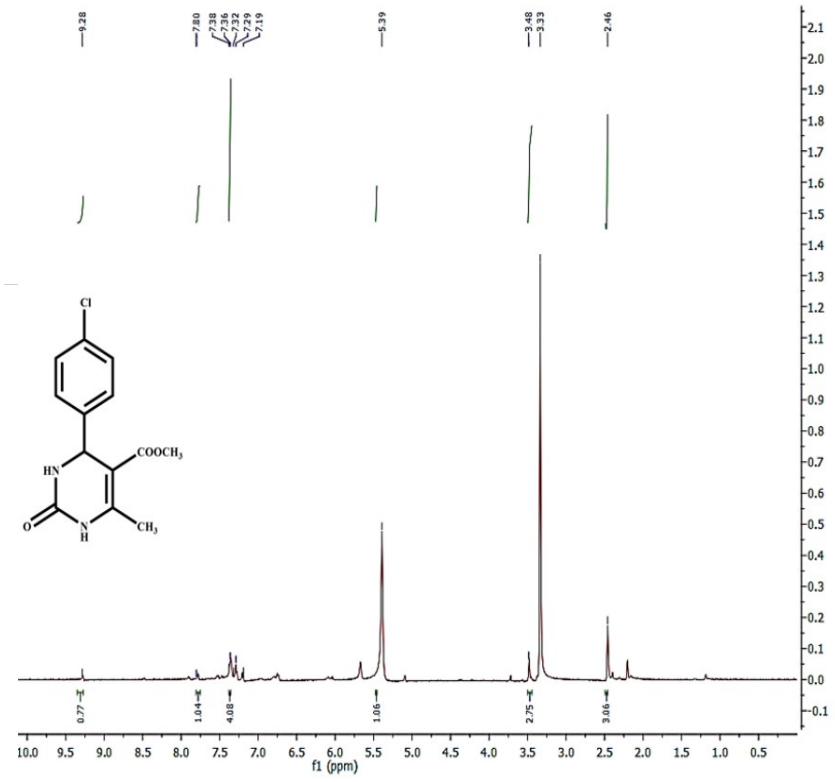


Fig. S9. ^{1}H-NMR spectrum of the compound **4c**.

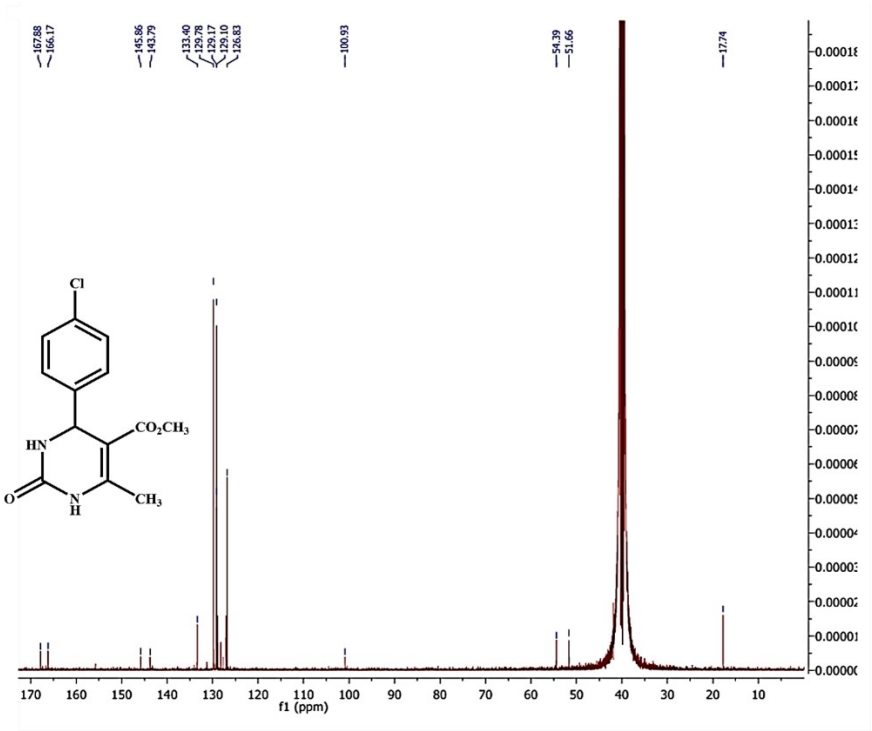


Fig. S10. ^{13}C-NMR spectra of compound **4c**.

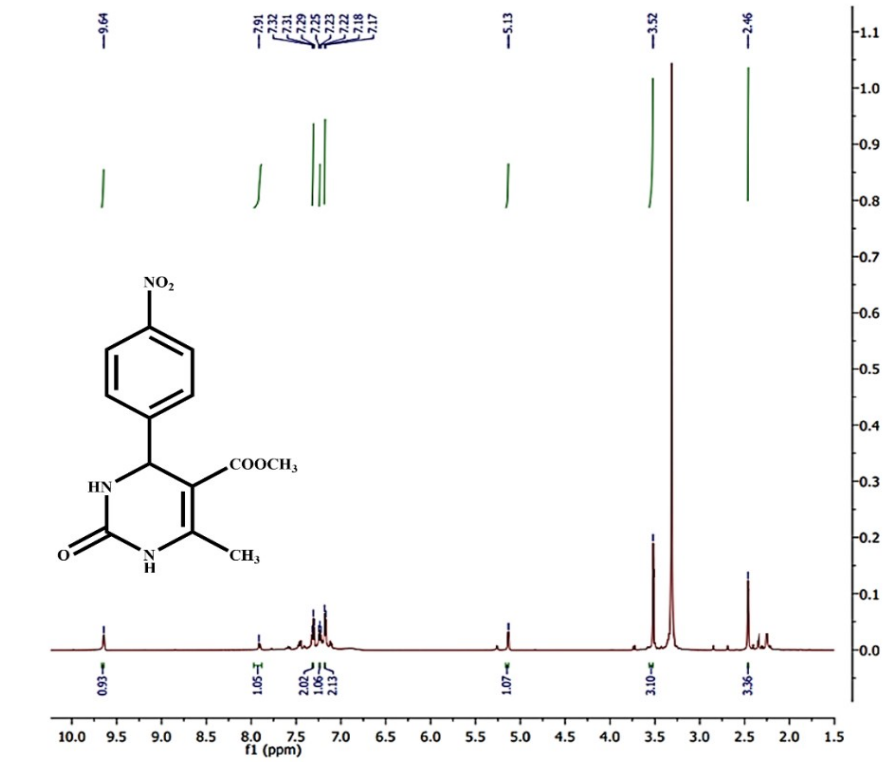


Fig. S11. ^{1}HNMR spectrum of the compound **4d**.

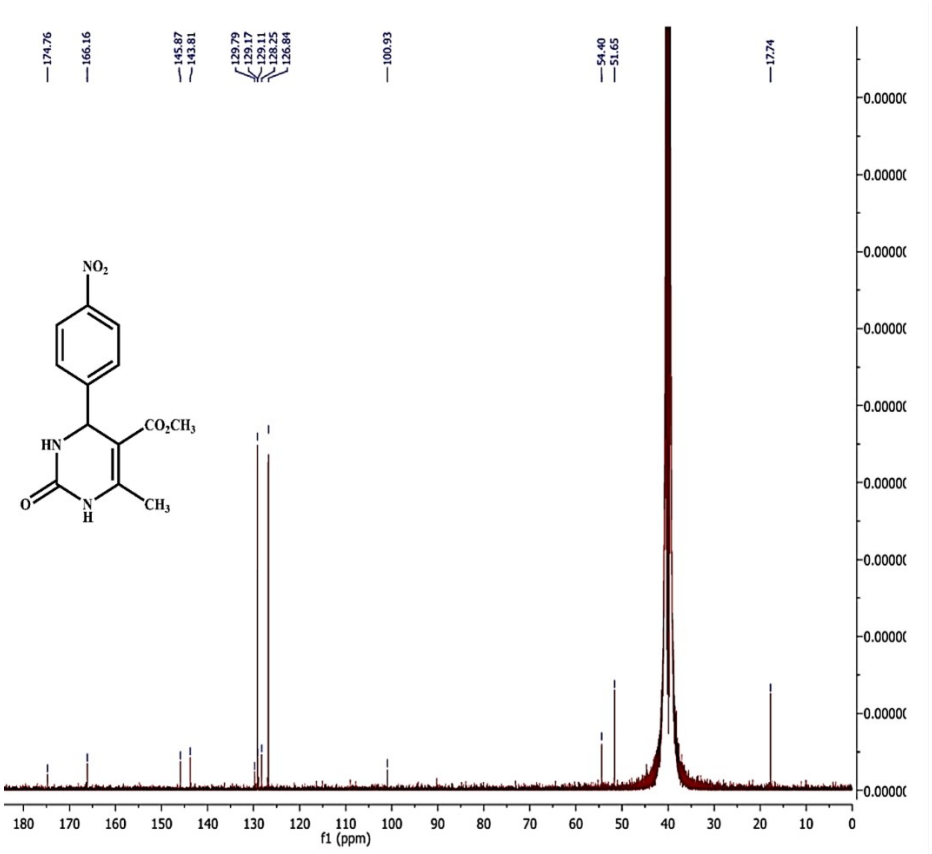


Fig. S12. ^{13}C-NMR spectra of compound **4d.**

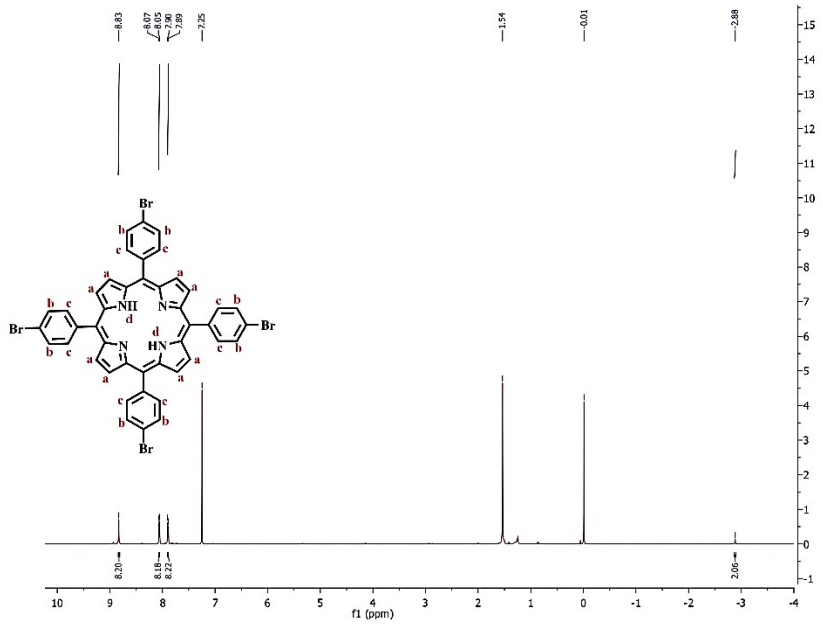


Fig. S13. ^{1}HNMR spectrum of the monomer tetrabromophenyl-porphyrin **(P)**.

10. Recyclability and chemical stability experiments

A recyclability experiment was carried out to evaluate the recyclability of the PBT photocatalyst during the regeneration of 1,4-NAD(P)H. In this experiment, we employed the same photocatalyst for five consecutive runs, equivalent to five cycles under identical reaction conditions. Our observations suggest that the photocatalytic efficiency remains almost constant throughout each recycling cycle, confirming the impressive stability of the PBT photocatalyst. Furthermore, XRD spectra of the PBT photocatalyst before and after five cycles of repeated 1,4-NADH regeneration was used to investigate the chemical stability of PBT photocatalyst, and no obvious difference exists between the two XRD spectra of the PBT photocatalysts.

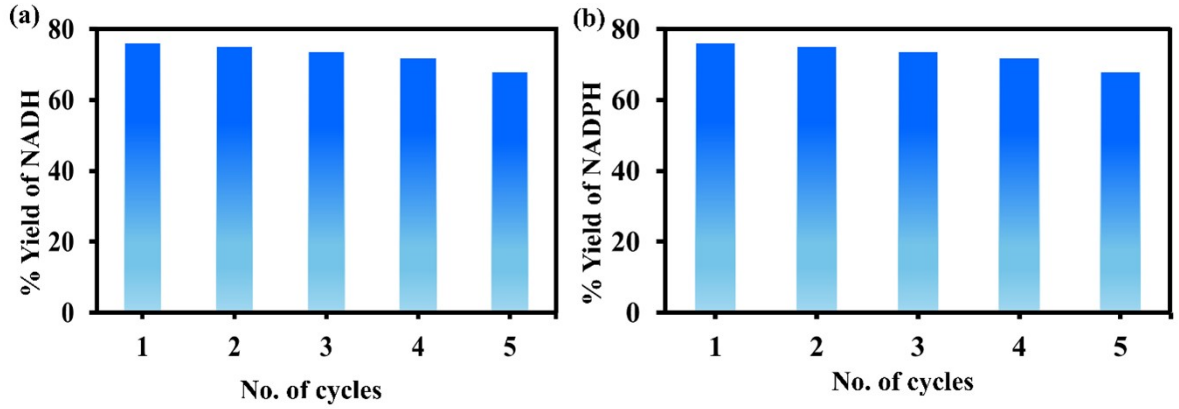


Fig. S14. Photocatalytic 1,4-NADH regeneration and (b) Photocatalytic 1,4-NADPH regeneration over multiple cycle (5 cycles) by use of PBT photocatalyst [β- NAD^+/$NADP^+$ (1.24 mmol), AsA (1.24 mmol), EM (0.62 mmol) and PBT photocatalyst (0.5 mg)].

11. Stability test of photocatalyst

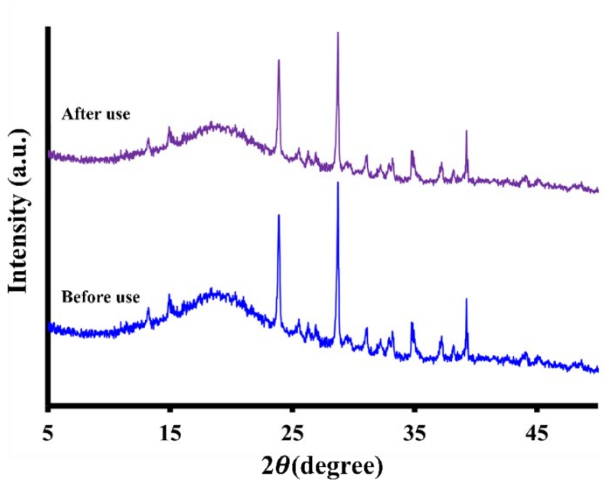


Fig. S15. Chemical stability of the PBT photocatalyst through XRD spectra.

12. UV-Visible absorption spectra for NAD(P)H regeneration

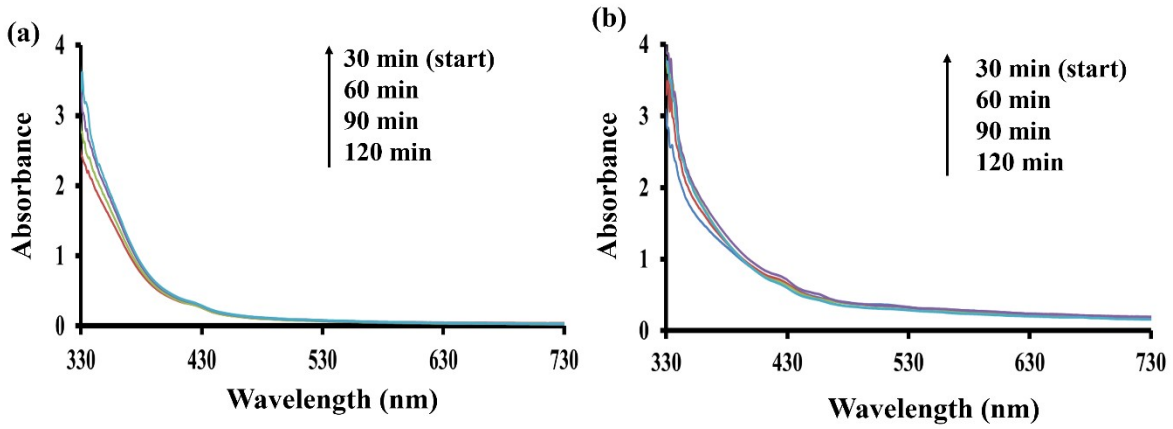


Fig. S16. UV-visible absorption spectra as a function of reaction time (a) NADH regeneration, and (b) NADPH regeneration. [9]

Reference:

1 **S. H. Lee, D. H. Nam, J. H. Kim, J.-O. Baeg and C. B. Park, *ChemBioChem*, 2009,** 10, **1621–1624.**

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