Electronic Supplementary Information (ESI)

Polystyrene Based Eosin Y as a Photocatalyst for Solar Light Mediated NADH/NADPH Regeneration and Organic Transformations

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1.General remarks

Sodium phosphate monobasic dihydrate (NaH_2PO_4. $2H_2O$), sodium phosphate dibasic dihydrate ($Na_2HPO_4.2H_2O$), nicotinamide adenine dinucleotide (NAD^+), nicotinamide adenine dinucleotide phosphate ($NADP^+$), aminomethyl polystyrene (P), eosin-Y (E), 2,2'-bipyridine, pentamethylcyclopentadienyl rhodium (III)($[Rh(C_5Me_5)\ Cl_2]_2$), N,N-dimethylformamide C_2H_5OH, HATU, DIEA, 1-vinylimidazole, 2-vinylpyridine, 4-vinyl pyridine, thiophenol, 2-amino-thiophenol, and 4-chlorothiophenol were purchased from sigma-aldrich.

2. Instruments and measurements

Shimadzu spectrophotometer (UV) and Bruker ALPHA-T FT-IR spectrometer were used for spectroscopy studies. Nano-zetasizer (NZS90) was used for zeta-potential and particle size studies. AFM~Brukermultimode, and SEM~FET Phillips instrument Model No. 200k VLAB6, FEL TECNAI G2 -20S-Twin were used for microscopy studies.

3. Synthesis of PBE photocatalyst:

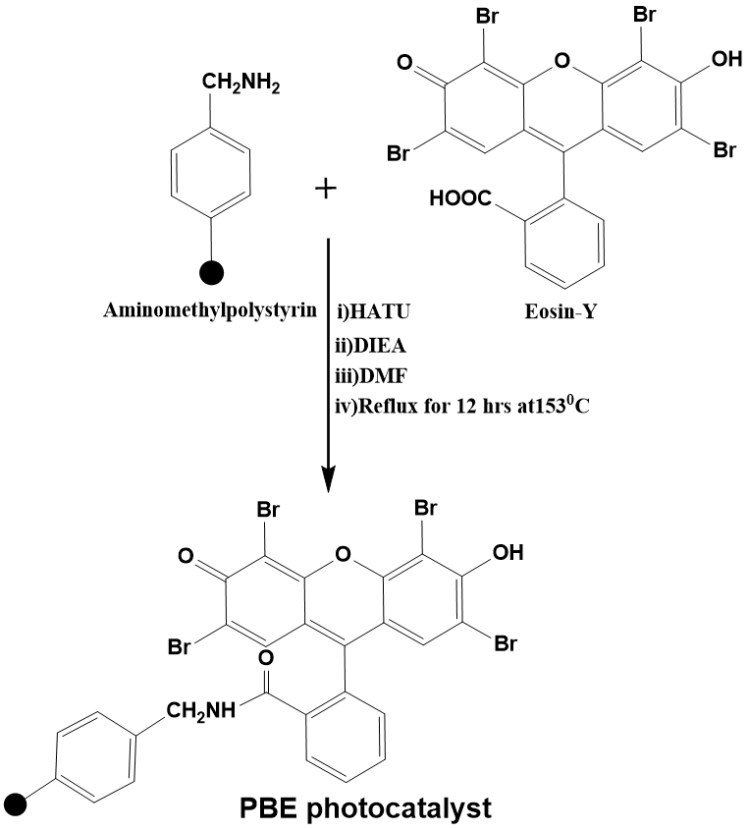

Figure S1. Synthesis of PBE photocatalyst.

4. Structure of PBE photocatalyst:

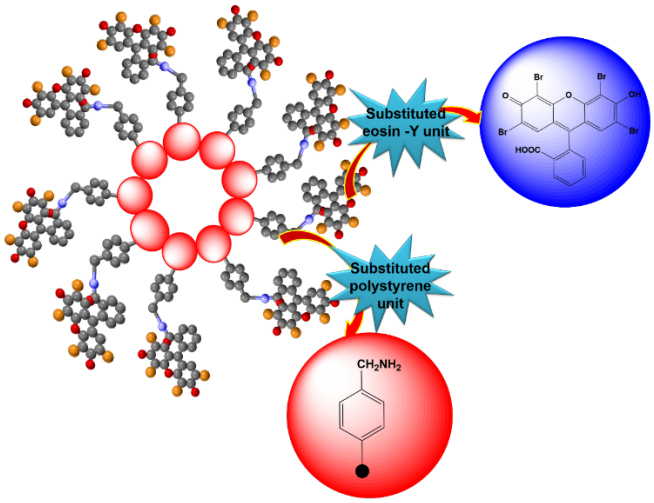

Figure S2. Structure of PBE photocatalyst.

5. Synthesis of Rh-complex $[Cp^*Rh(bpy)Cl]^+$:

The Rh-complex was synthesized as per the reported method.[1] Initially, 25 mg of Rh-compound ($[Rh(C_5Me_5)Cl_2]_2$) was dissolved in 5mL distilled methanol under an N_2 atmosphere. Consequently, 13 mg of 2, 2'-bipyridyl (2eq.) was added to the above solution and then the solution was stirred at room temperature in the dark condition. After that addition of diethyl ether, a yellow color precipitate was formed. Lastly, the obtained product was filtered and dried at ambient temperature under N_2 atmosphere (Figure S3).

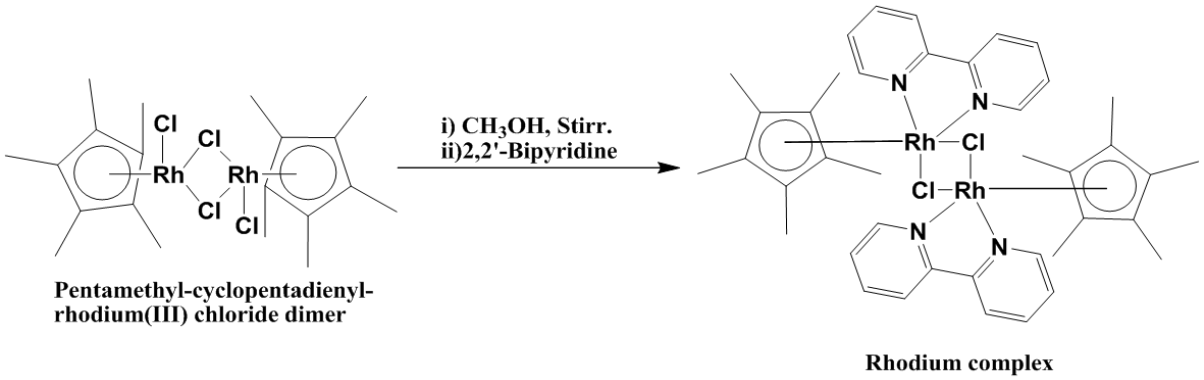

Figure S3. Synthesis of Rh-complex.

6. Reusability test of PBE photocatalyst for photocatalytic regeneration of NADH/NADPH from $NAD^+/NADP^+$:

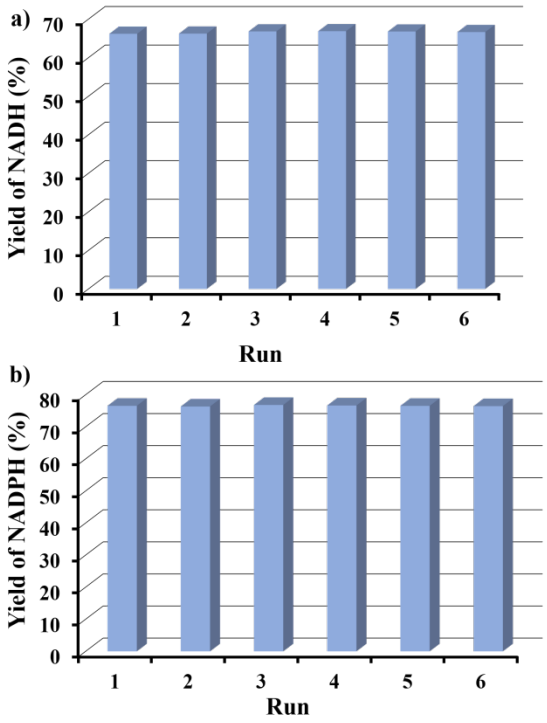

Figure S4. Five-time reusability test of PBE photocatalyst under solar-light mediated photoregeneration of (a) NADH, and (b) NADPH respectively. Reaction conditions: 2387µL sodium phosphate buffer (pH ~ 7.0, 0.1M), 31µL PBE photocatalyst, 248 µLof $NAD^+/NADP^+$, 124 µLof [Cp*Rh(bpy)Cl]Cl and 310 µL of ascorbic acid of under nitrogen atmosphere at room temperature (see details in experimental section of the manuscript). The reaction time for NADH/NADPH regeneration was set for 120 min and yields were calculated for each run and shown here.

7. Reusability test of PBE photocatalyst for solar light mediated sulfoxide synthesis:

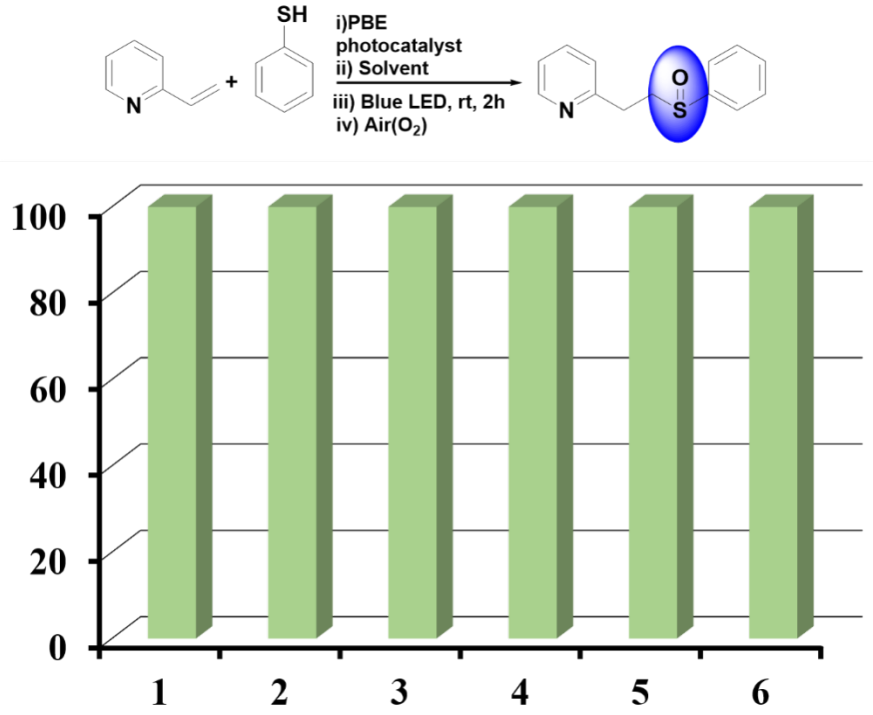

Figure S5. Reusability test of PBE photocatalyst for solar-light mediated sulfoxide synthesis of alkene with thiophenol.

8. DFT calculations

The molecular structures of eosin Y and its bound form with a single unit of polystyrene were energetically optimized by density functional theory (DFT) with B3LYP functional and a basis set of 6-31G(d, p). We employed the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)in order to describe the solvation environment. Vibrational frequencies of all the optimized structures were calculated to check that the optimized structures have no imaginary frequencies. To investigate the excited-state characters of eosin Y and its bound form, we implemented the time-dependent density functional theory (TD-DFT) calculations with two different functional of B3LYP and ωB97XD. All the calculations were performed using the Gaussian 16 package.[2] After the TD-DFT calculation, natural transition orbital (NTO) analysis[3] was employed to assign the character of each excited state and to show the shift in electron density upon electronic excitation. The theoretical absorption spectra and the excited electron-hole pairs obtained from NTO analysis are summarized in Figure S6-S7. Since the excited-state character of

Eosin Y bound with polystyrene moieties can be influenced by the length of polystyrene moieties, we designed the eosin Y molecules bound with the two and three units of polystyrene. Using those structures, we implemented the optimizations with the same level used in eosin Y and the TD-DFT calculations with ωB97XD functional and a basis set of 6-31G(d, p) as shown in Figure S6.

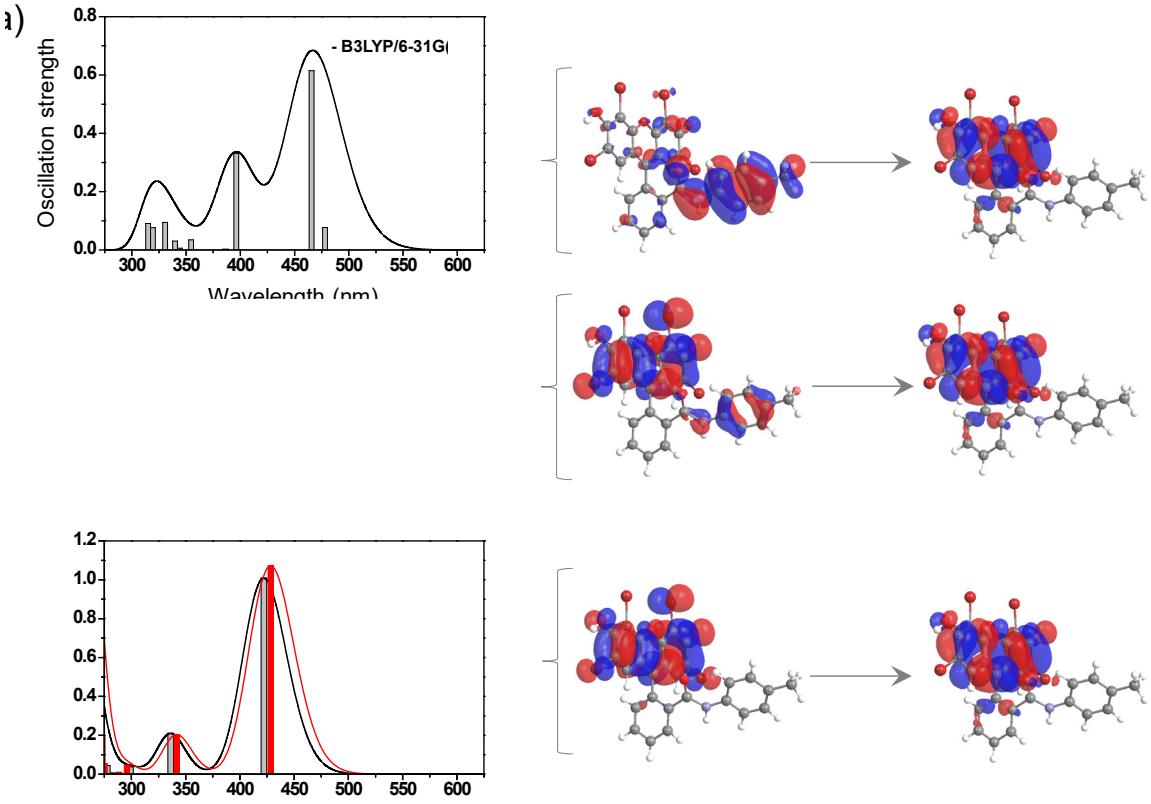

Figure S6. TD-DFT calculations of eosin Y bound to a single unit of polystyrene. (a, b) Results from the TD-DFT calculation with B3LYP functional and a basis set of 6-31G (d, p). (a) Theoretical absorption spectrum and (b) natural transition orbitals corresponding to the lowest and the second lowest transitions. (c, d) Results from the TD-DFT calculations with ωB97XD functional and two different basis sets. (c) Theoretical absorption spectra calculated from the basis sets of 6-31G(d, p) (black) and def2-TZVP (red) and (d) natural transition orbitals corresponding to the lowest transition in the level of ωB97XD/def2-TZVP.

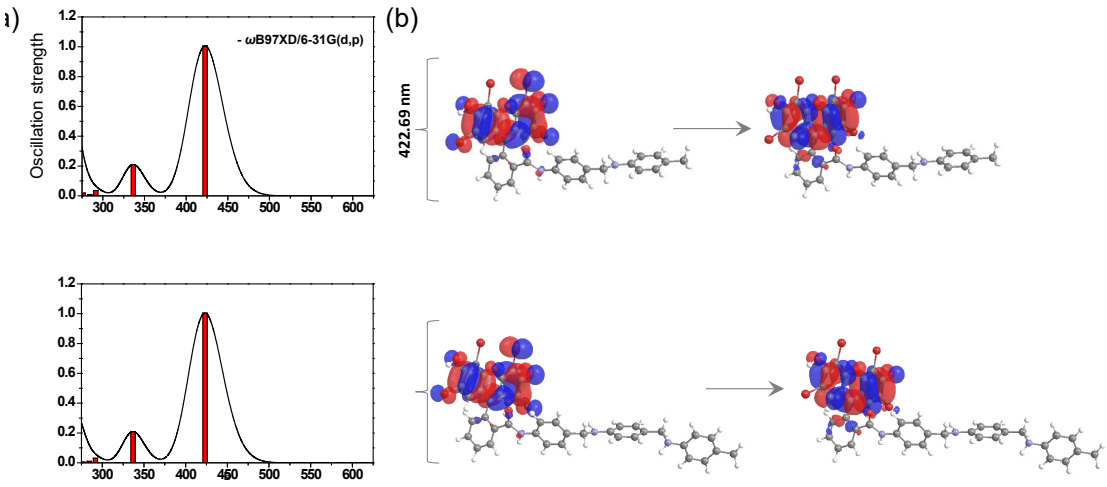

Figure S7. TD-DFT calculations of eosin Y bound to extended units of polystyrene. (a, b) TD-DFT calculation of eosin Y bound to two units of polystyrene by using ωB97XD functional and a basis set of 6-31G (d, p). (a) Theoretical absorption spectrum and (b) natural transition orbitals corresponding to the lowest transition. (c, d) Results from the TD-DFT calculations with ωB97XD functional and two different basis sets. (c, d) Results from the eosin Y bound to three units of polystyrene. (c) Theoretical absorption spectrum and (d) natural transition orbitals corresponding to the lowest transition.

9. Scanning electron microscopy study:

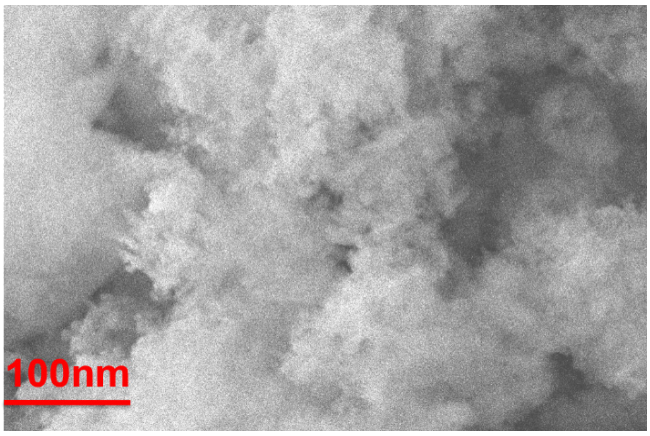

Figure S8. Scanning electron microscopy images of eosin-Y

10. Particle size studies

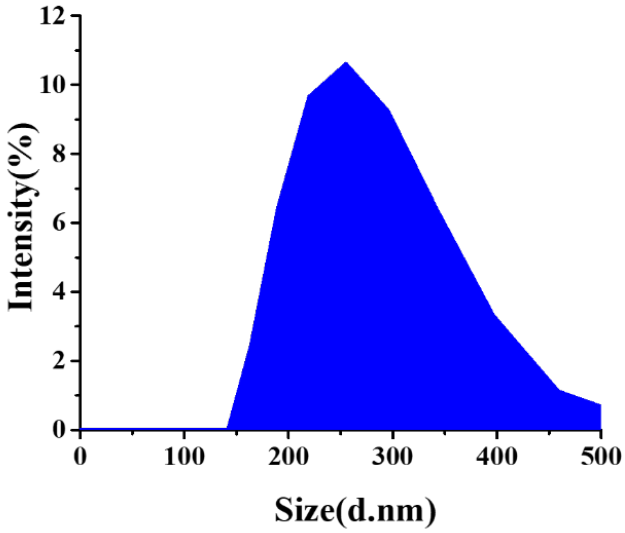

Figure S9: Particle size analysis of eosin-Y

11. Zeta potential analysis:

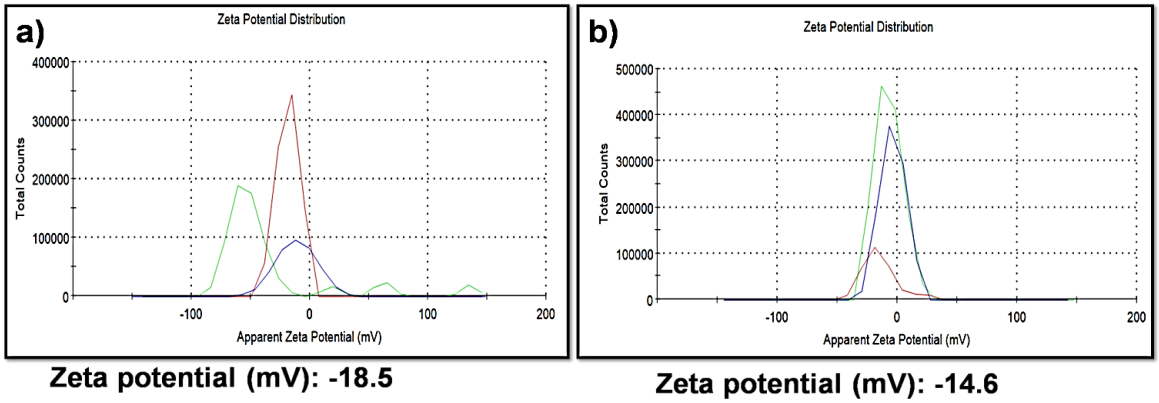

Figure S10: Zeta potential analysis of (a) PBE, and (b)P photocatalysts.

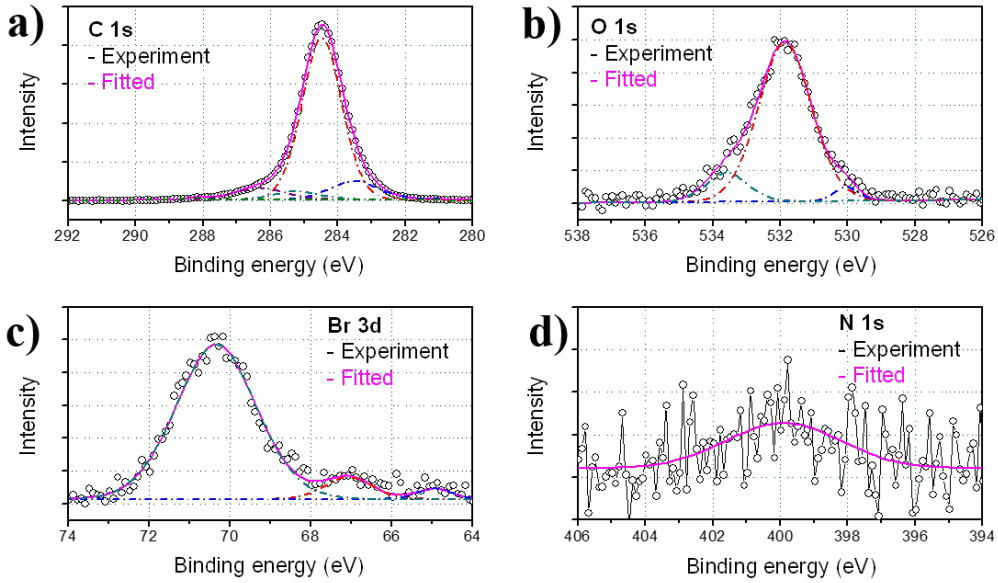

Figure S12. X-ray photoelectron spectroscopic data of PBE photocatalyst sample. The experimental data (black circles) were fitted with the multiple Gaussian functions (color-coded).

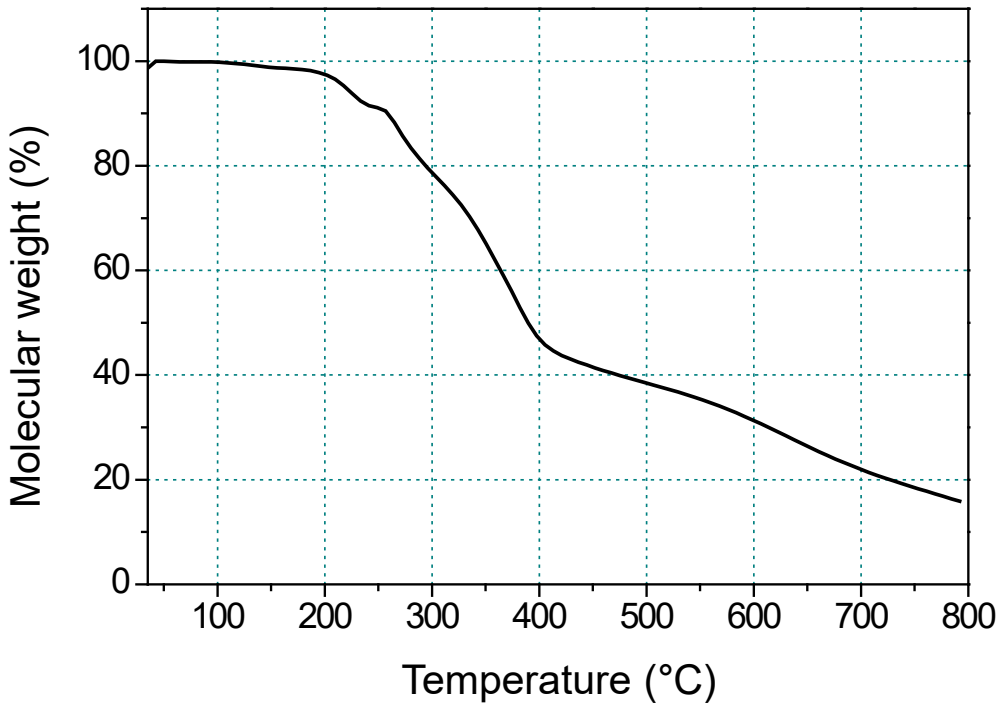

Figure S13. Thermogravimetric analysis (TGA) of PBE photocatalyst.

Table 1. Literature survey for the NADH regenerations and the organic transformations by comparing with the results from our work

Entry	Photocatalyst	NADH regeneration(%)	Sulfoxidation Yield (%)	Ref
1.	$W_2Fe_4Ta_2O_{17}$	60	……	4
2.	Fmoc-FF/g-C_3N_4	62.7	……	5
3.	Proflavine	63.4	……	6
4.	Tio_2	……..	97	7
5.	Rose Bengal	…….	89	8
6.	P-Rose Bengal	……	99	9
7.	$[PO_4\{WO(O_2)_2\}_4]$@ImPIILP	……..	95	10
8.	PBE photocatalyst	65.19%	99.8	Our Work

12. SI References

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