Electronic Supplementary Information (ESI)

Conjugated HCl-doped polyaniline for Photocatalytic Oxidative Coupling of Amines under Visible Light

Peng Kong,[ab] *Pei Liu,*[ab] *Zhenyu Ge,*[c] *Hao Tan,*[bd] *Linjuan Pei,*[bd] *Jie Wang,*[bd] *Pengqi Zhu,*[bd] *Xianmo Gu,*[b] *Zhanfeng Zheng*[*b] *and Zhong Li*[*a]

a. Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Institute of Coal Chemical Engineering, Taiyuan University of Technology, 79 West Yingze Street, Taiyuan 030024, P. R. China

b. State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, P. R. China

c. School of Material Science and Engineering, Shandong University, 27 Shanda Nanlu, Jinan 250100, P. R. China

d. University of Chinese Academy of Sciences, Yuquan Road, 19(A), Beijing 100049, P. R. China

*Corresponding author: Emails: zfzheng@sxicc.ac.cn; lizhong@tyut.edu.cn

Table S1. Porosity data of the PANIs.

PANIs	S_{BET} (m^2/g)	Pore Size (nm)	Pore Volume(cm^3/g)
PANI-ES	30.8	12.6	0.10
PANI-EB	46.6	13.3	0.16
PANI-LB	133.5	9.3	0.31
PANI-PB	68.2	15.3	0.26

Table S2. Contribution of nitrogen groups resulting from the fitting of Gaussian components to the N 1s photoelectron spectra

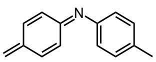
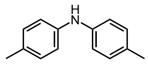
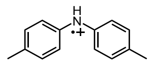
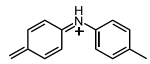
PANIs				
	398.7 eV	399.8 eV	401.0 eV	401.9 eV
PANI-ES	12.0	56.0	23.6	8.4
PANI-EB	35.4	55.8	0	8.8
PANI-LB	12.9	79.2	0	7.9
PANI-PB	6.0	26.2	7.2	60.6

Table S3. The optimization result of different interaction of ESII with benzylamine by DFT/6-311G+(p,d).

System	Charge	Spin	$\Delta E^{[a]}$ (eV)
ESII-1	+1	Doublet	-0.726
ESII-2	+1	Doublet	-0.449
ESII-3	+1	Doublet	0.949

[a] Interaction energy (ΔE) for complex formation has been determined using equation: $\Delta E = E_{cox} - E_{cot}$, where E_{cox} and E_{cot} are optimized energy of complex and individual components, respectively.

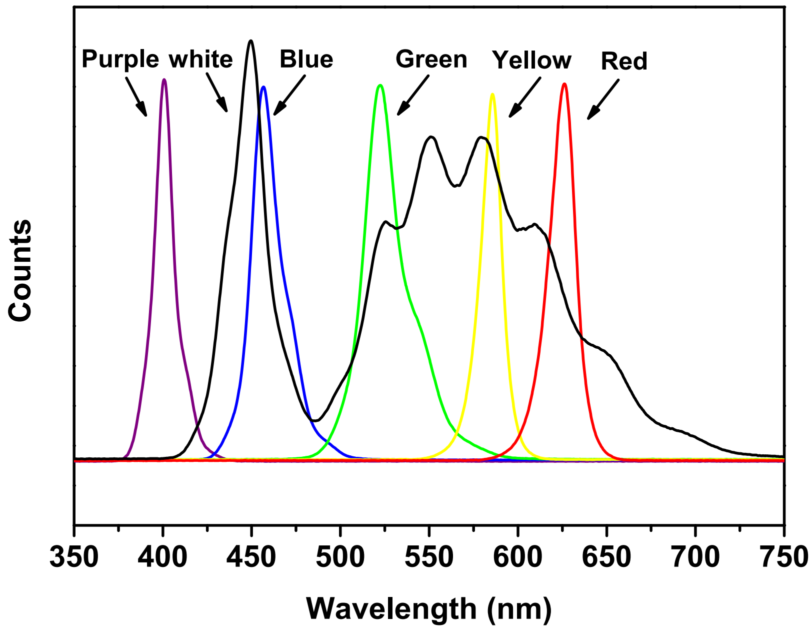


Figure S1. The output spectra of incandescent lights used for the reaction: 100 W LED light (white and colored).

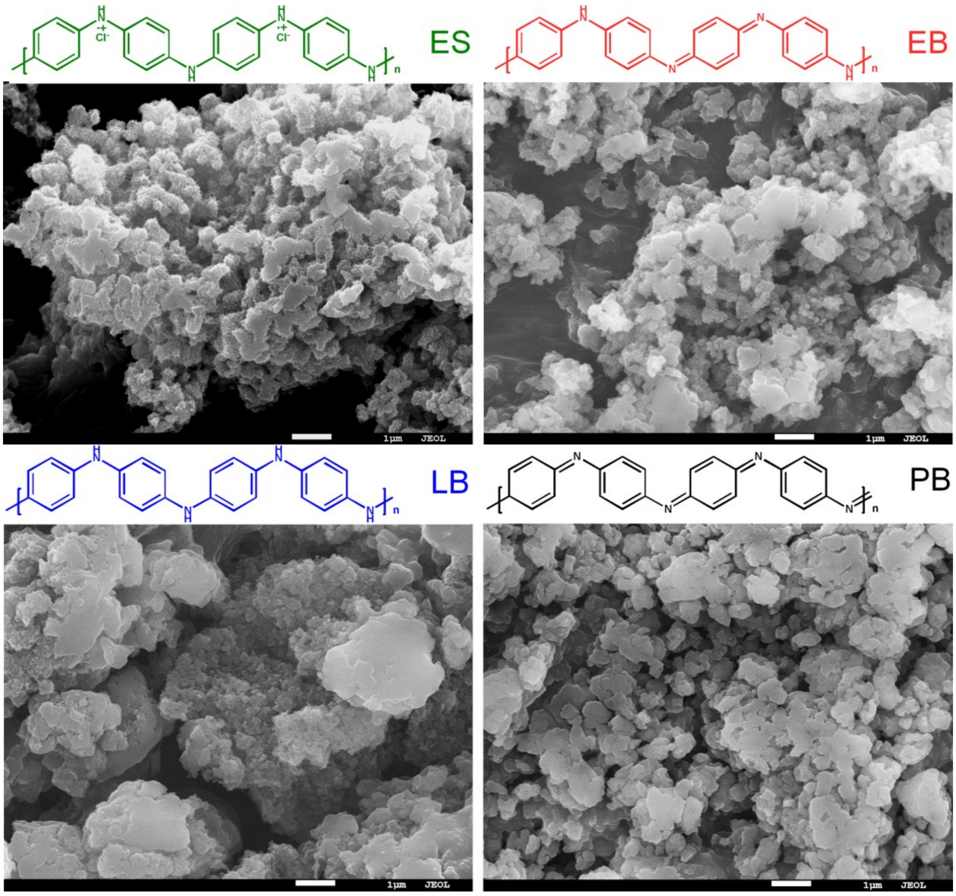


Figure S2. SEM images of PANI-ES, PANI-EB, PANI-LB and PANI-PB. The molecular formulas of four different oxidation states of PANI are displayed above the SEM pictures respectively. The scale bars are all 1μm.

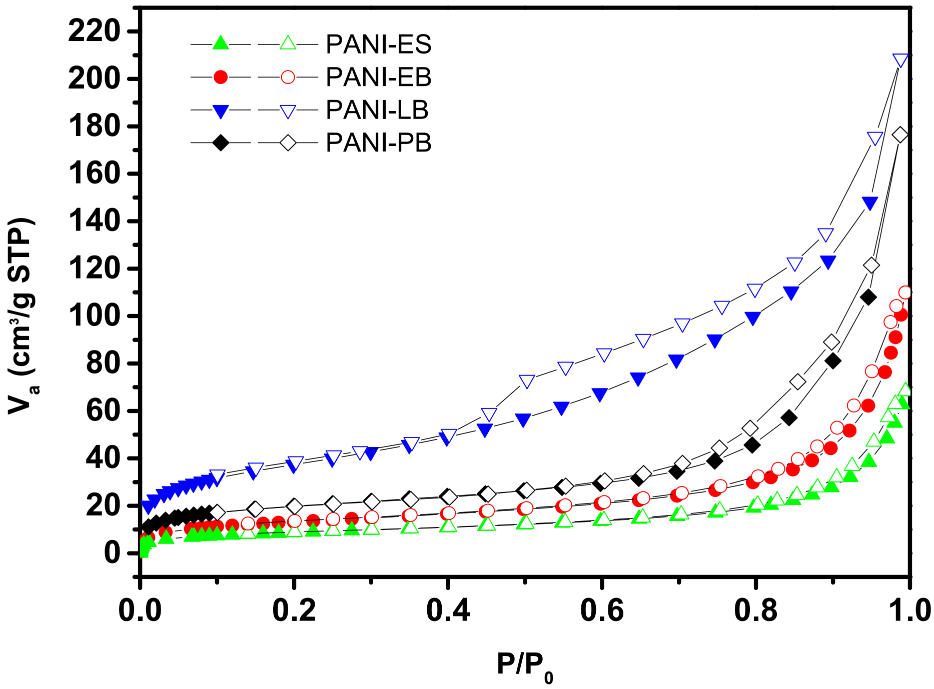


Figure S3. N_2 gas adsorption/desorption isotherm of PANIs (closed: adsorption (●), open: desorption (○)).

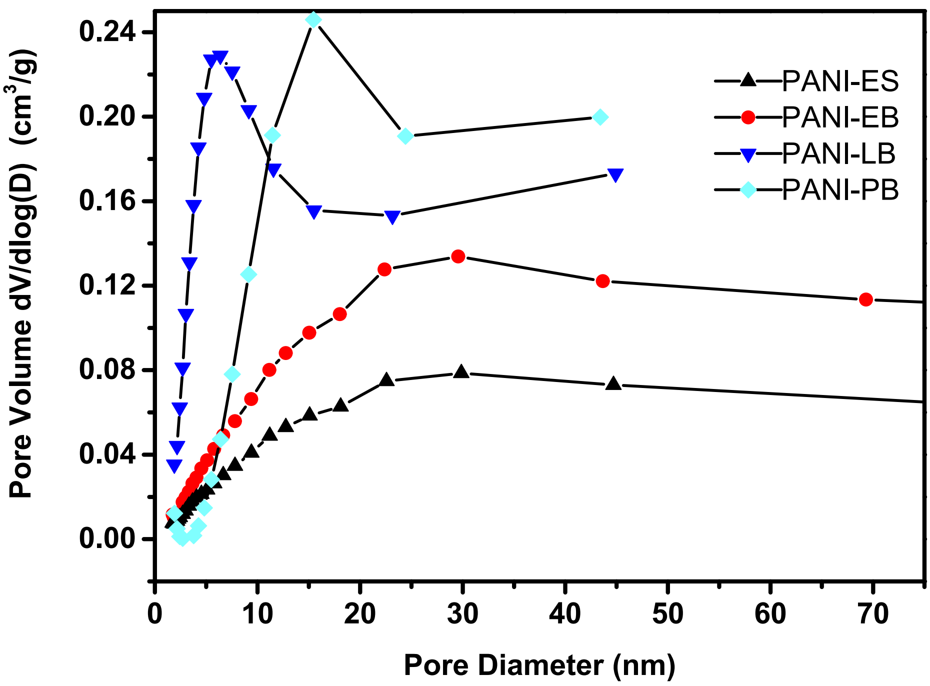


Figure S4. Pore size distribution of the PANIs.

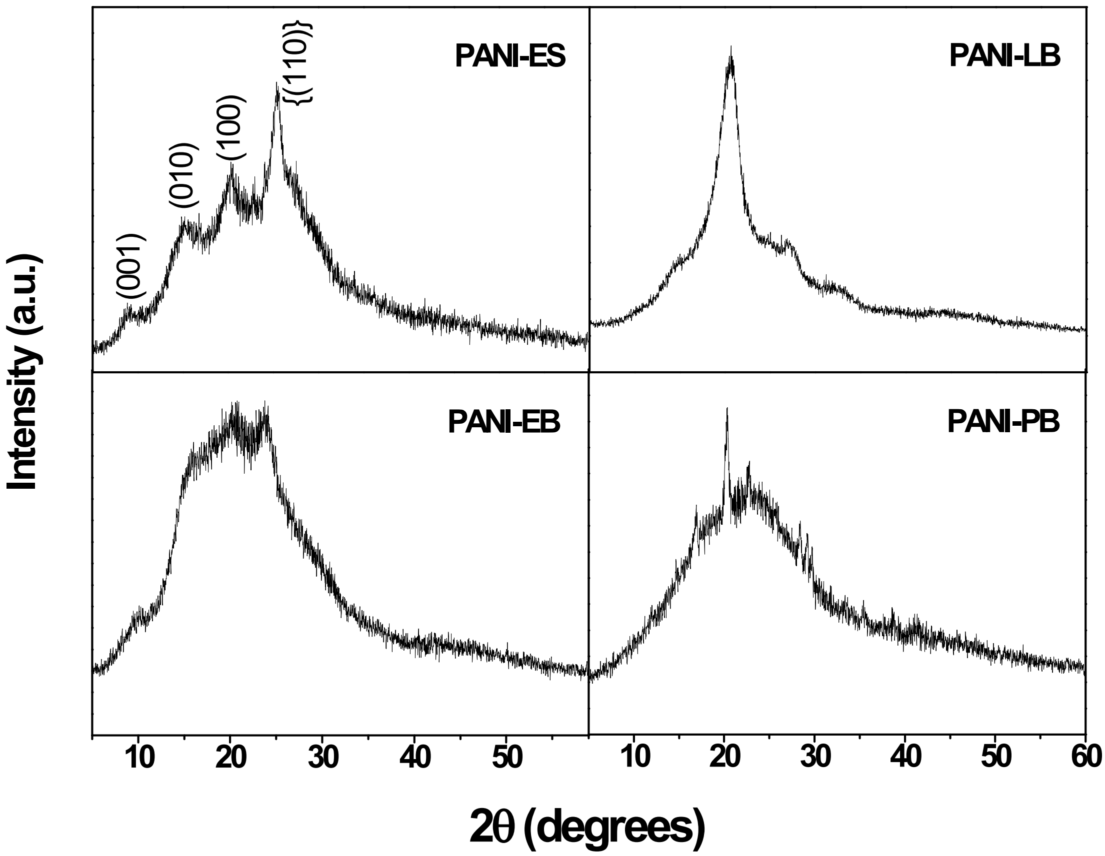


Figure S5. XRD patterns of the PANIs.

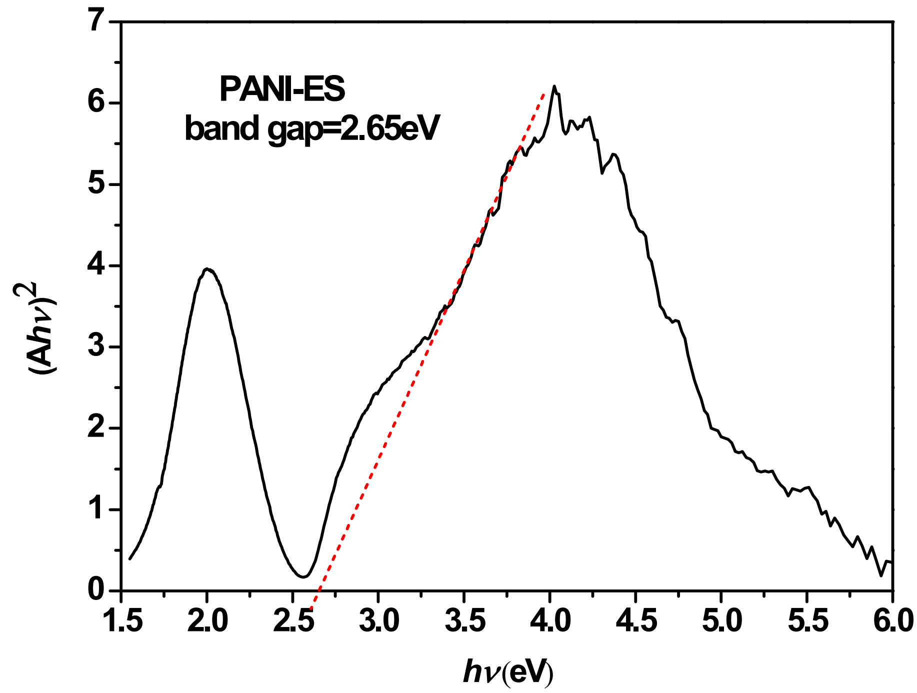


Figure S6. Plot of $(Ahv)^2$ versus *hv* for PANI-ES.

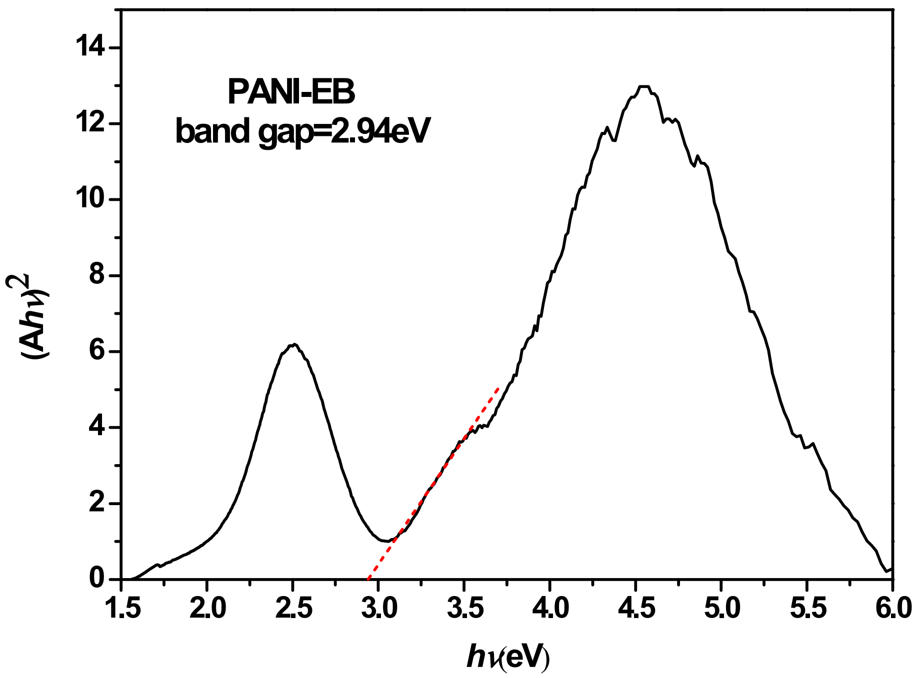


Figure S7. Plot of $(Ahv)^2$ versus *hv* for PANI-EB.

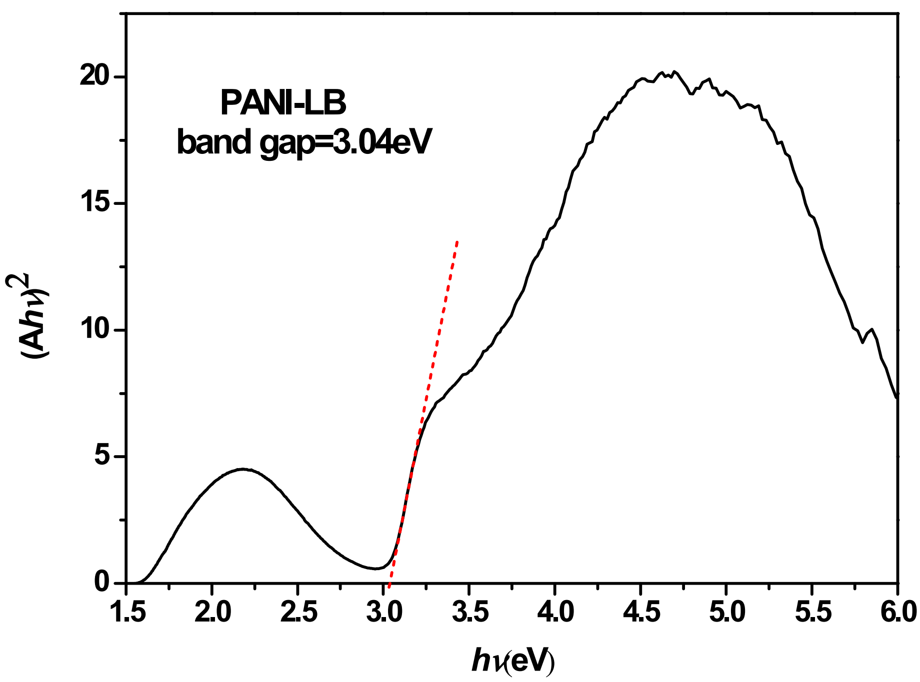


Figure S8. Plot of $(Ahv)^2$ versus *hv* for PANI-LB.

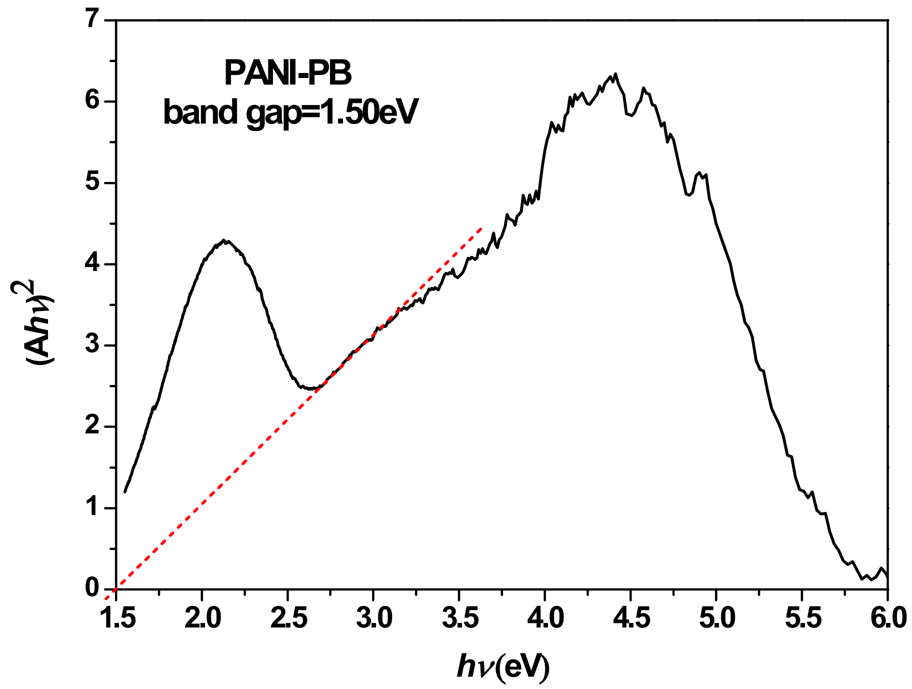


Figure S9. Plot of $(Ah\nu)^2$ versus $h\nu$ for PANI-PB.

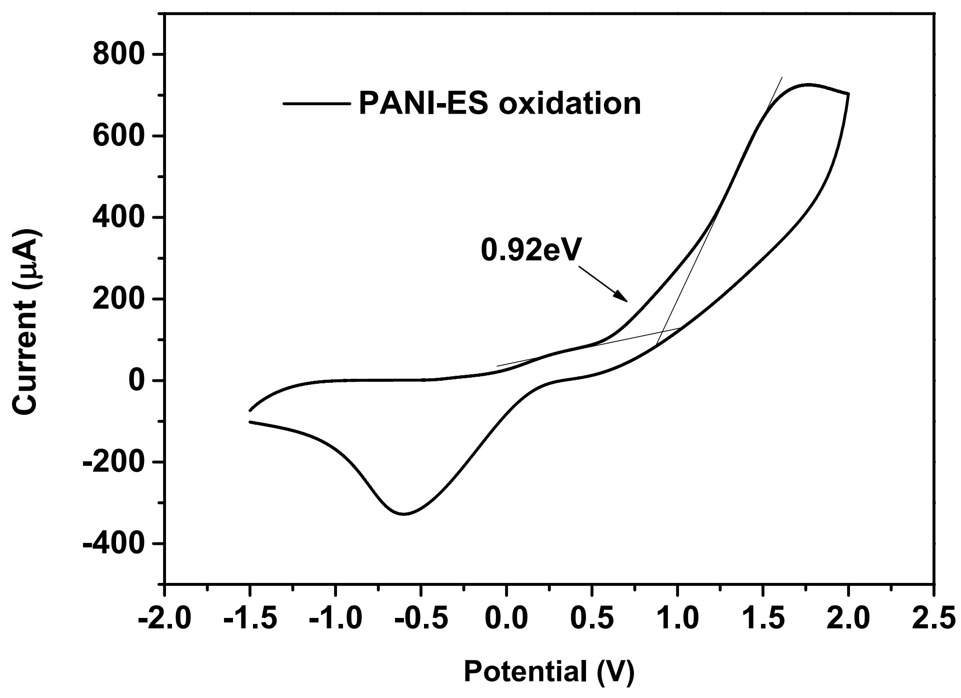


Figure S10. Cyclic voltammograms of PANI-ES.

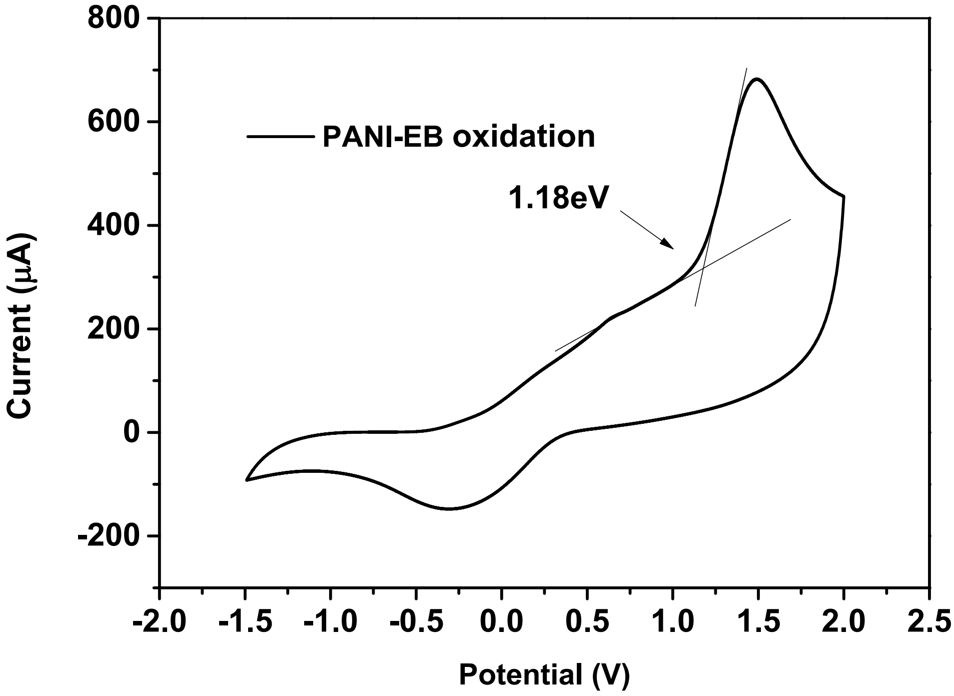


Figure S11. Cyclic voltammograms of PANI-EB.

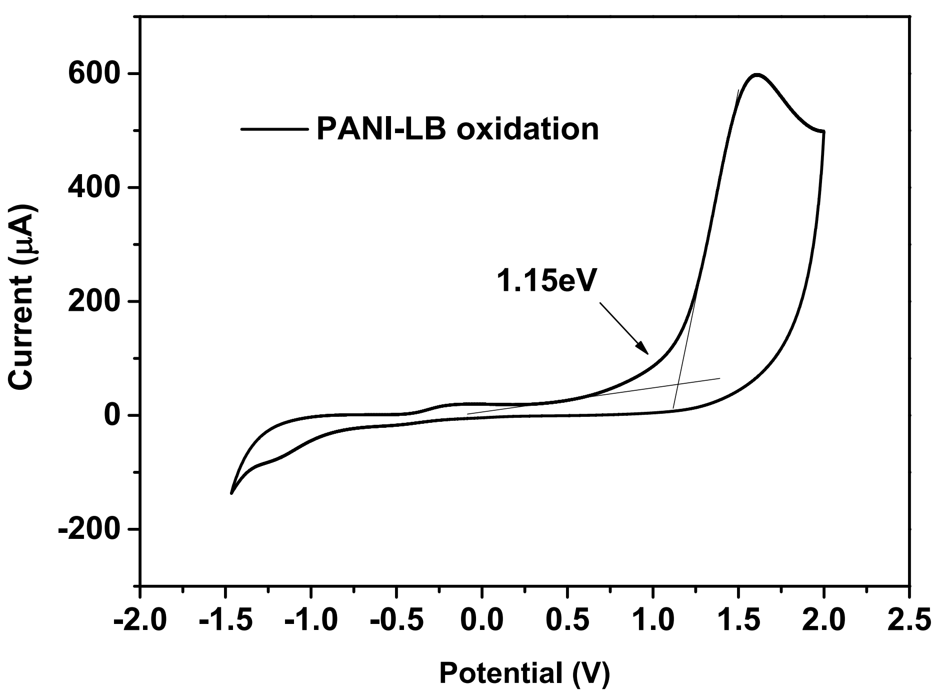


Figure S12. Cyclic voltammograms of PANI-LB.

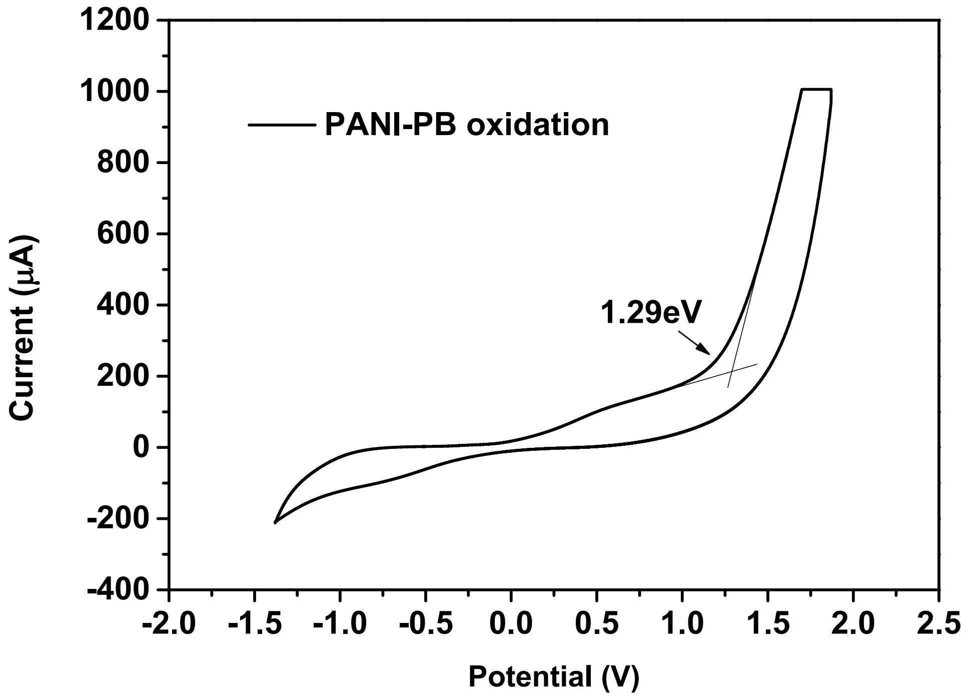


Figure S13. Cyclic voltammograms of PANI-PB.

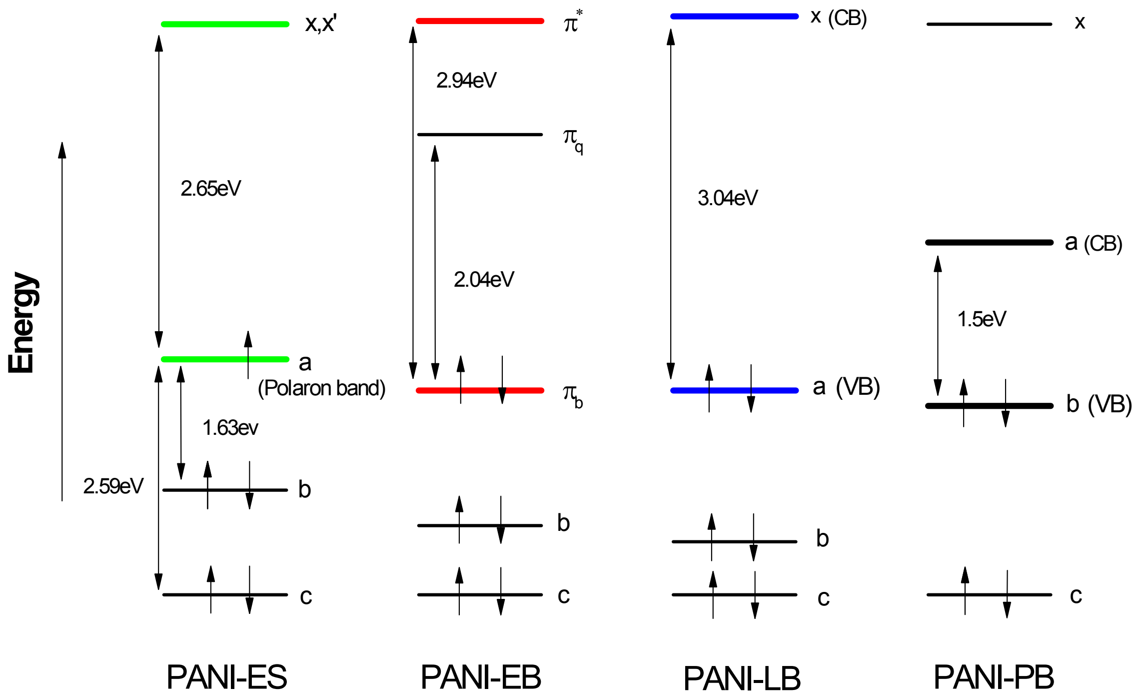


Figure S14. Schematic energy level diagrams of PANI-ES, PANI-EB, PANI-LB and PANI-PB (CB, conduction band; VB, valence band)

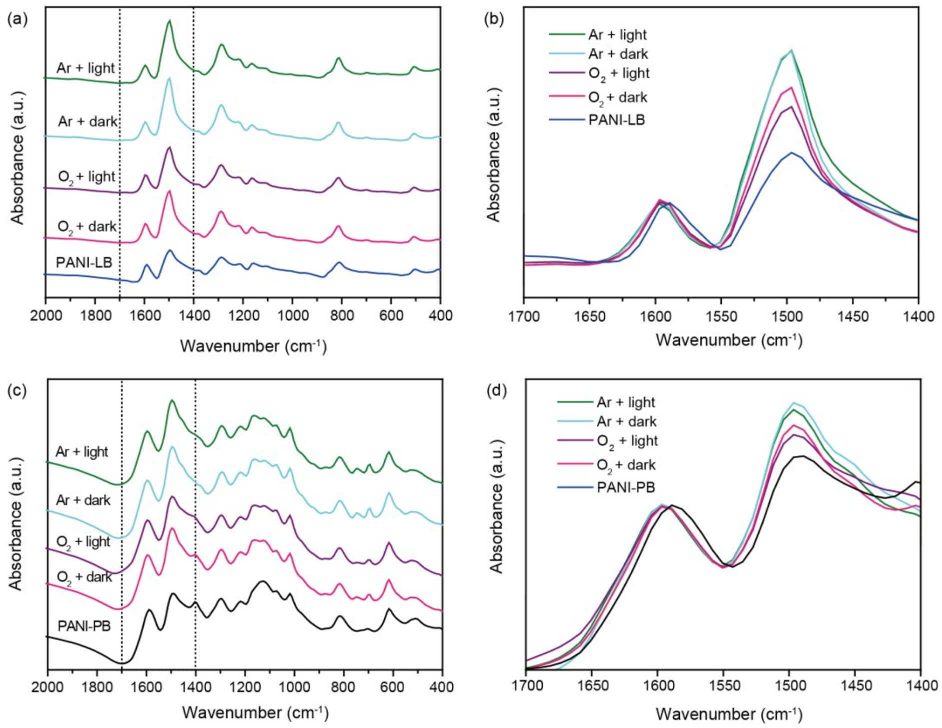


Figure S15. FT-IR spectra of a) PANI-LB and catalysts after reaction under different condition, b) enlargement dotted part in picture a, c) PANI-PB and catalysts after reaction under different condition, d) enlargement dotted part in picture c.

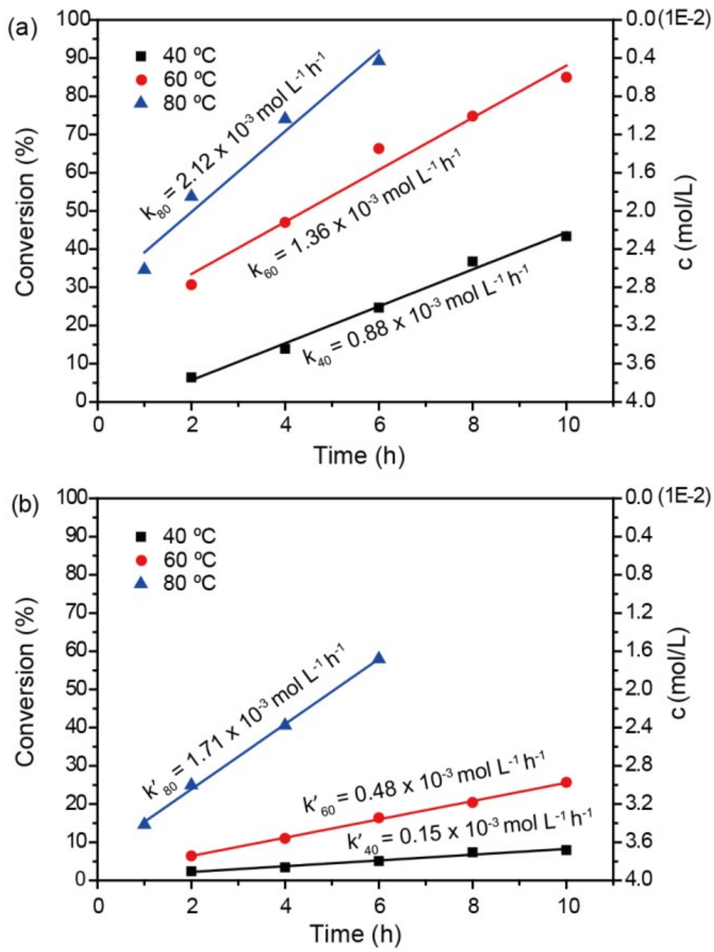


Figure S16 Reaction profiles for the selective oxidation of benzylamine over PANI-ES at different temperatures (40, 60 and 80 °C): a) under visible light irradiation, b) in the absence of light.

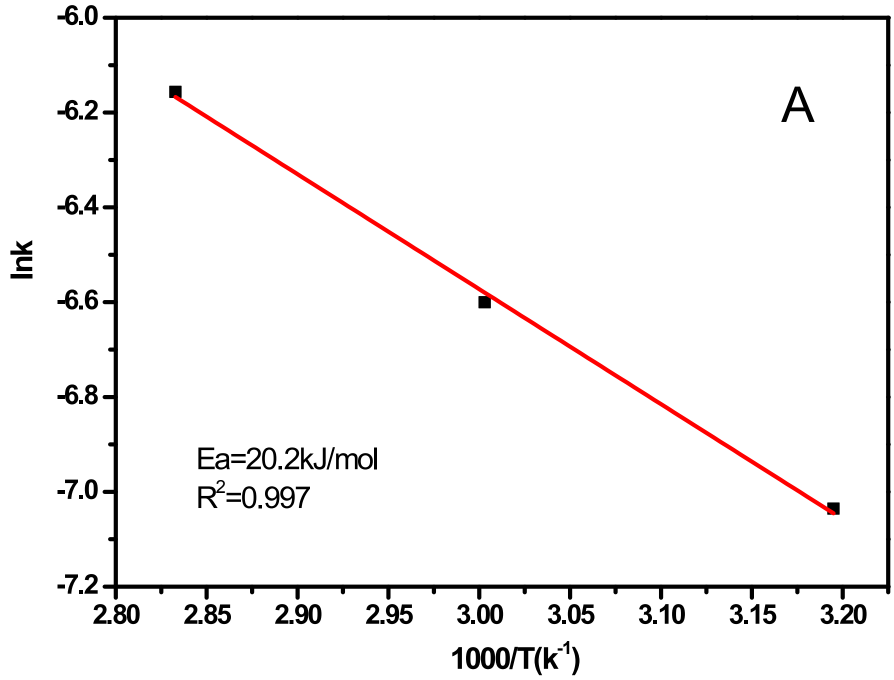


Figure S17. Linear fitting of ln(k) versus 1000/T in the selective oxidation of benzylamine over PANI-ES under visible light irradiation.

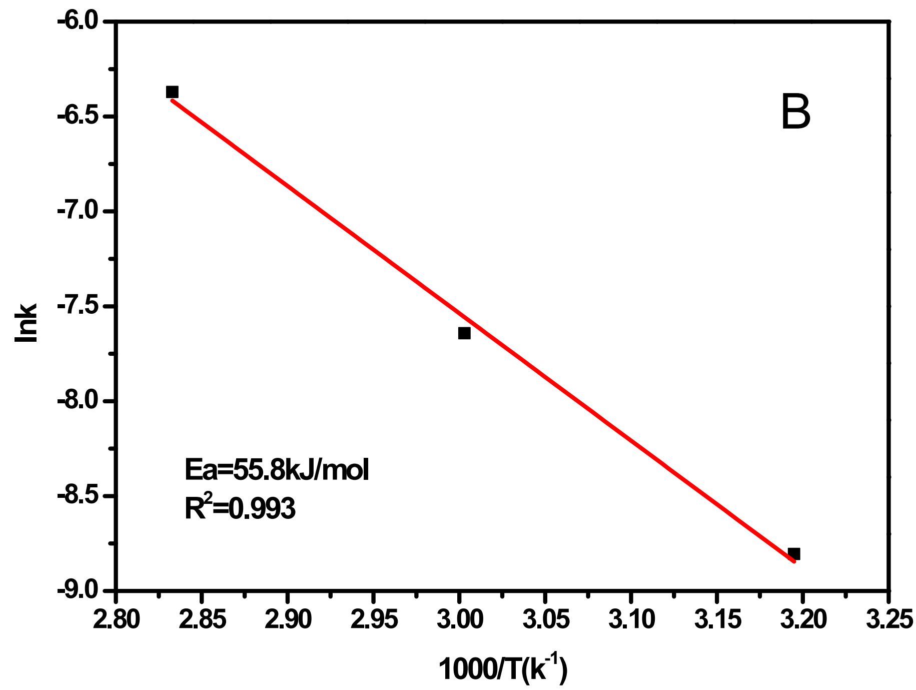


Figure S18. Linear fitting of ln(k) versus 1000/T in the selective oxidation of benzylamine over PANI-ES in the dark.

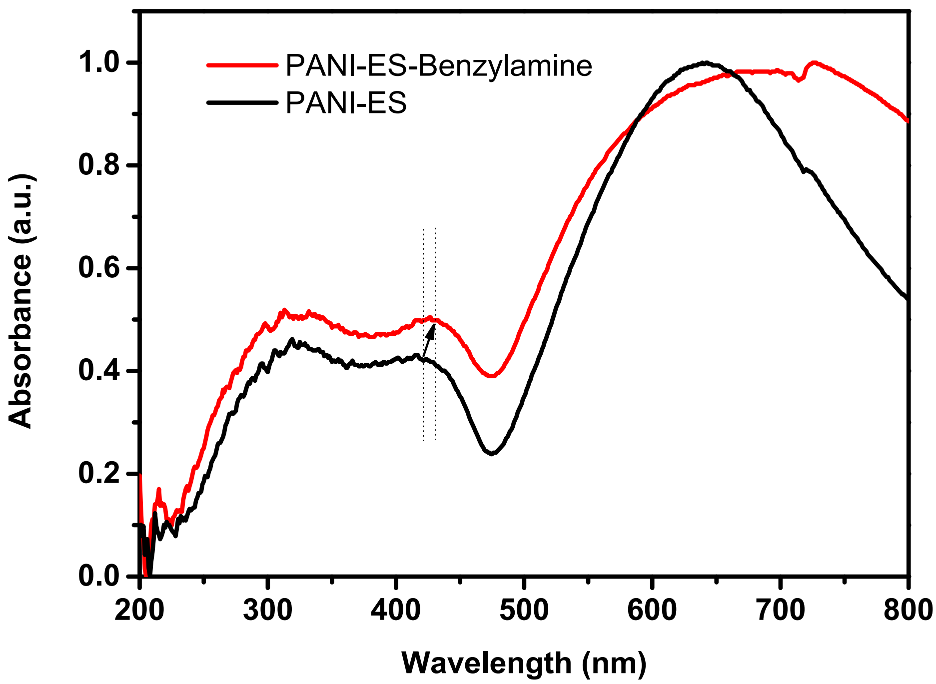


Figure S19. UV-Vis absorption spectra of PANI-ES and PANI-ES-Benzylamine.

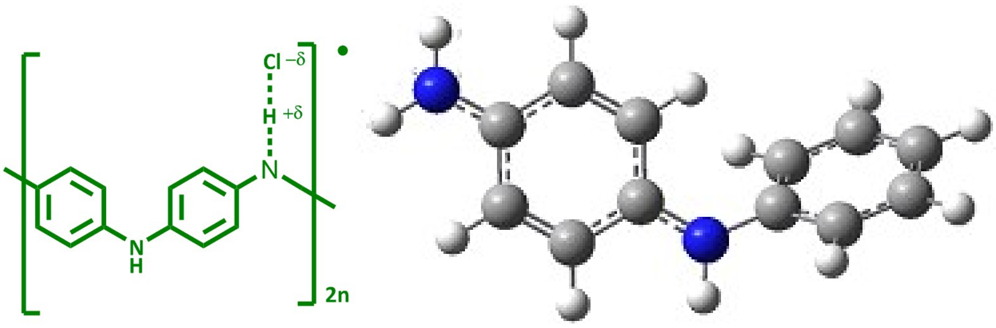


Figure S20. Polaron structure of HCl-doped polyaniline (ESII).

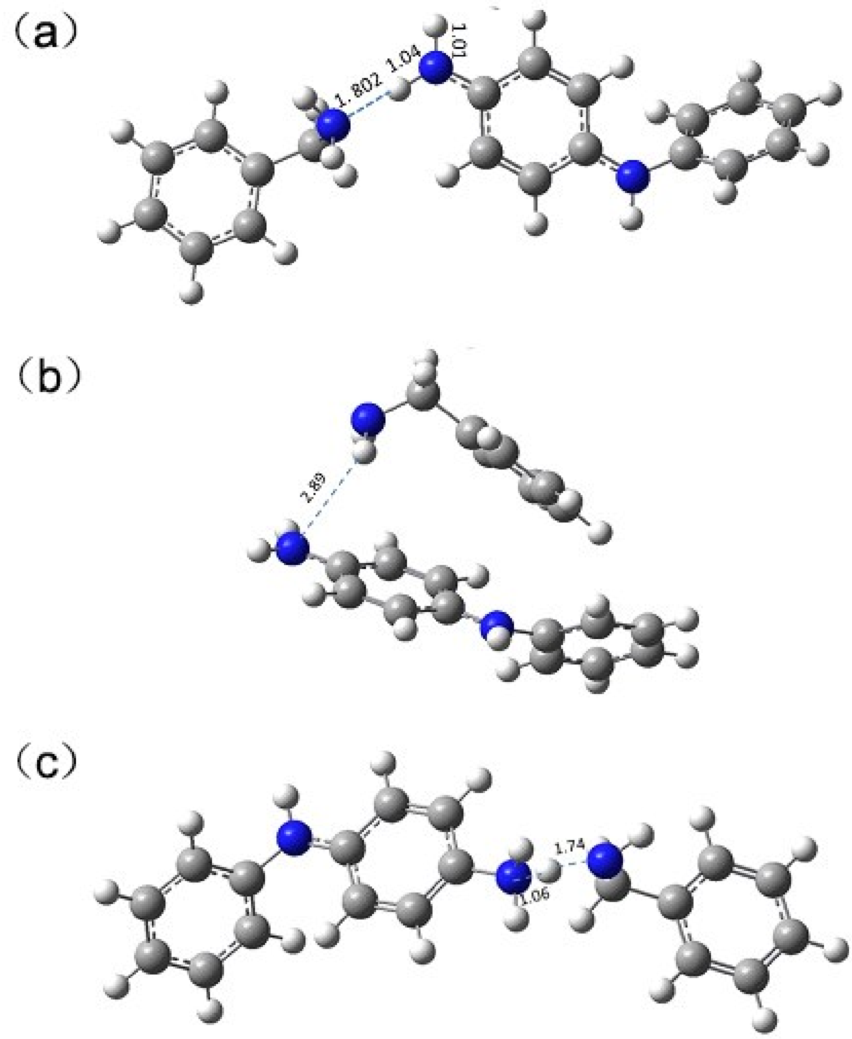


Figure S21. Optimized geometry of (a) ESII-1, (b) ESII-2 and (c) ESII-3, Gray represents Carbon, White represents Hydrogen, and Blue represents Nitrogen. The number is the distance between two atoms in the unit of angstrom.

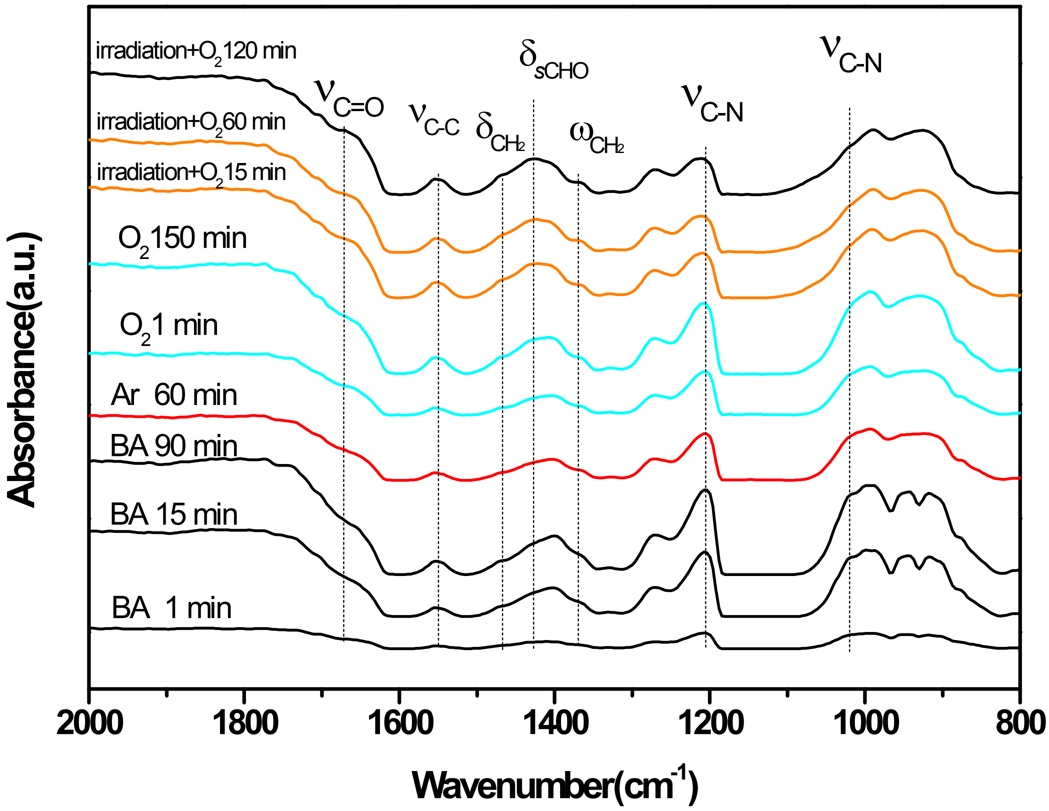


Figure S22. Time course in situ FT-IR spectra of PANI-ES after expose to benzylamine (BA) vapour at 25 Pa and after irradiation under a dry oxygen atmosphere.

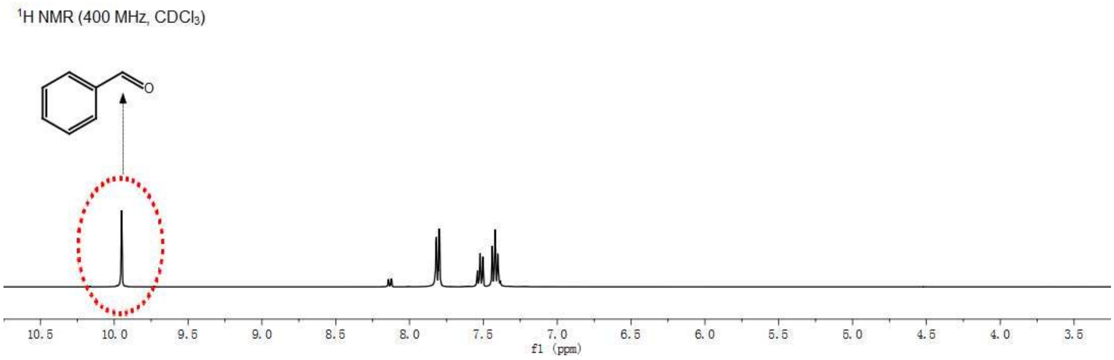


Figure S23. ^{1}H NMR spectrum of benzaldehyde (analytical pure, Aladdin Reagent (Shanghai) Co., Ltd). The peak at ca.10 ppm is attributed to aldehyde hydrogen of benzaldehyde.

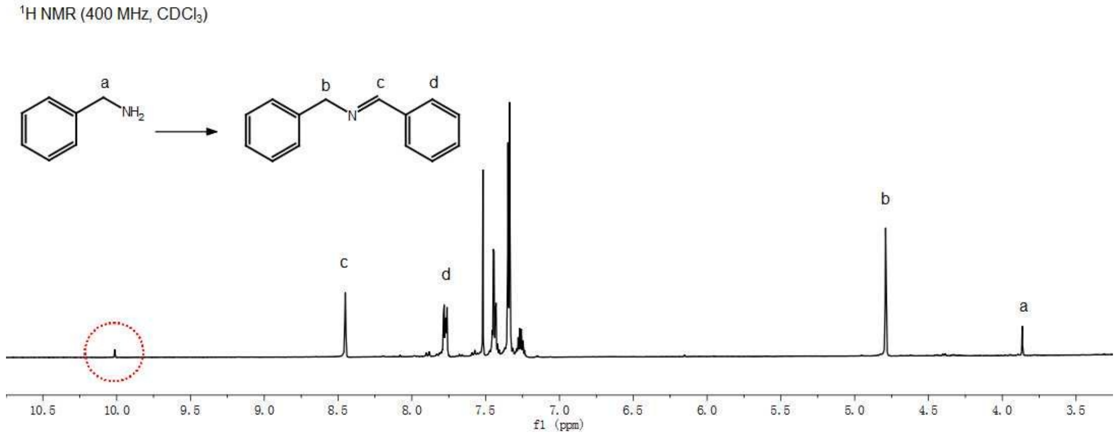


Figure S24. ^{1}H NMR spectrum of the reaction products. Reaction conditions: 0.2 mmol benzylamine, 50 mg of catalyst, 5 mL of CH_3CN, 10h, 1 atm O_2, 60 °C, white LED 0.4 W/cm^2.

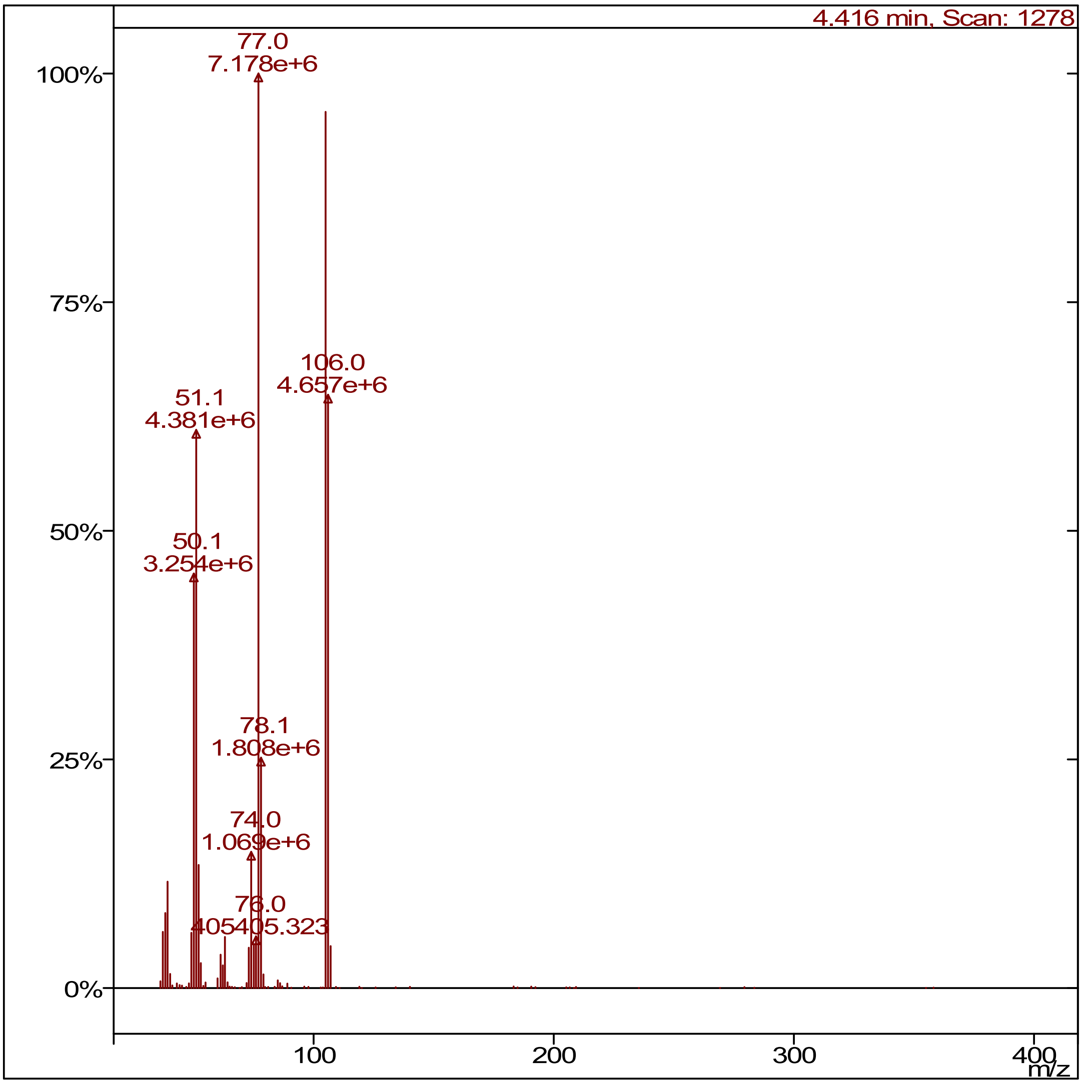


Figure S25. Mass spectrum of the intermediate product.

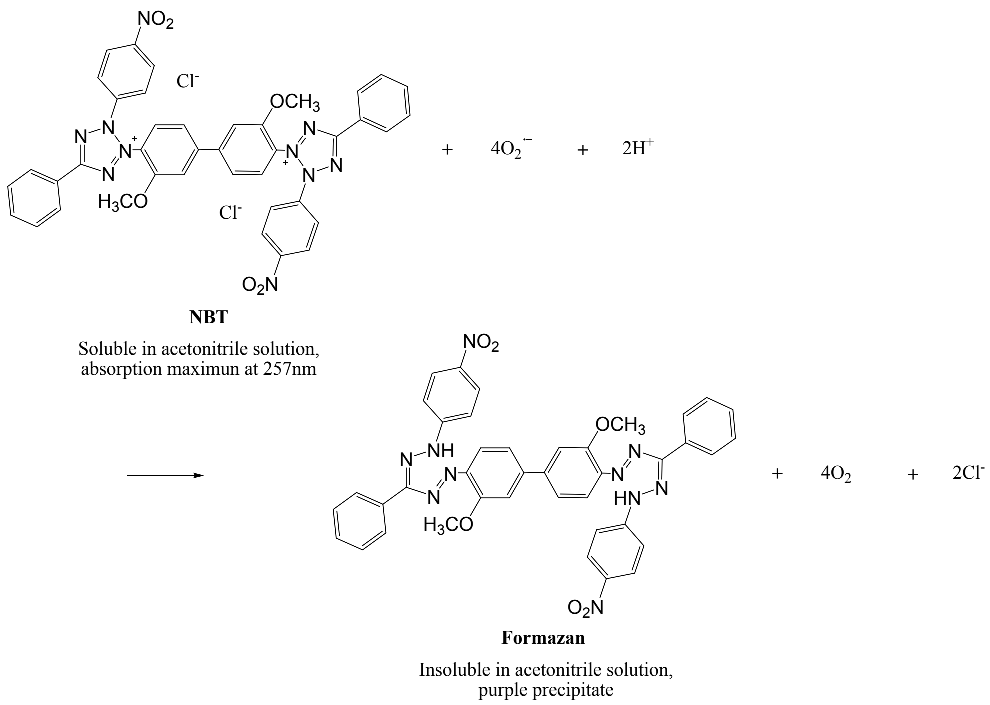


Figure S26. Reaction of NBT with superoxide ion.

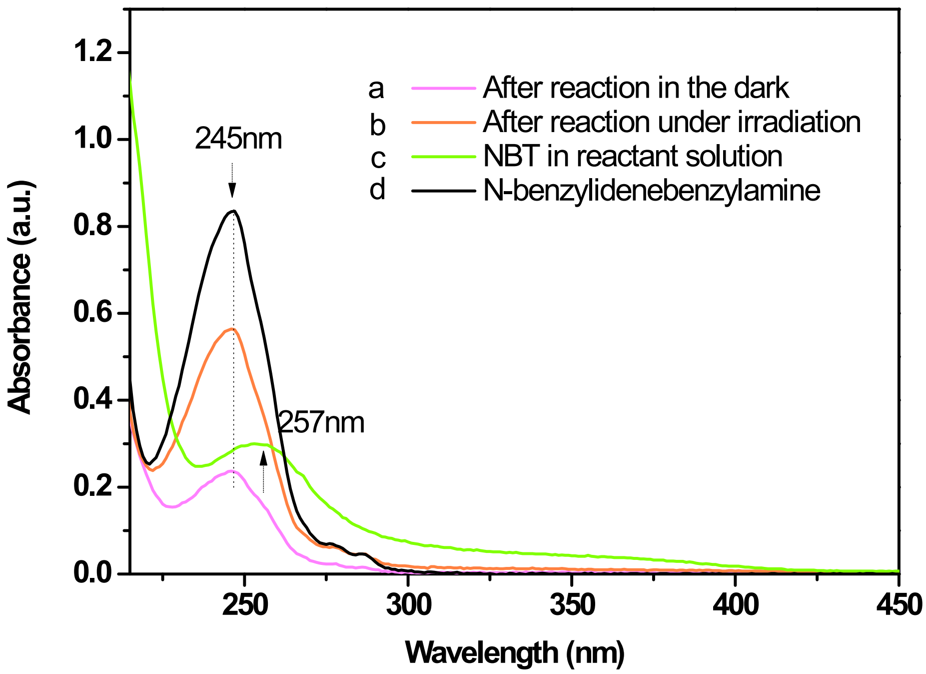


Figure S27. UV-Vis absorption spectra of a) NBT in reactant solution, b) suspension after reaction in the dark, c) suspension after reaction under irradiation and d) N-benzylidenebenzylamine.

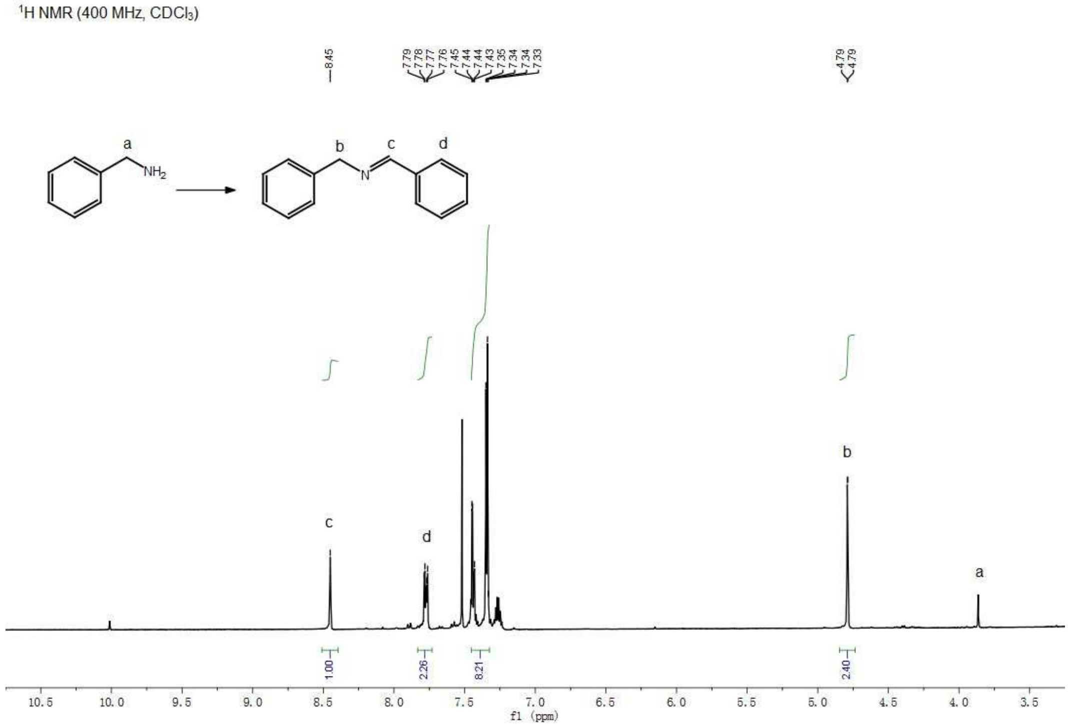


Figure S28a. ^{1}H NMR spectrum of the reaction product using benzylamine as substrate in Table 2.

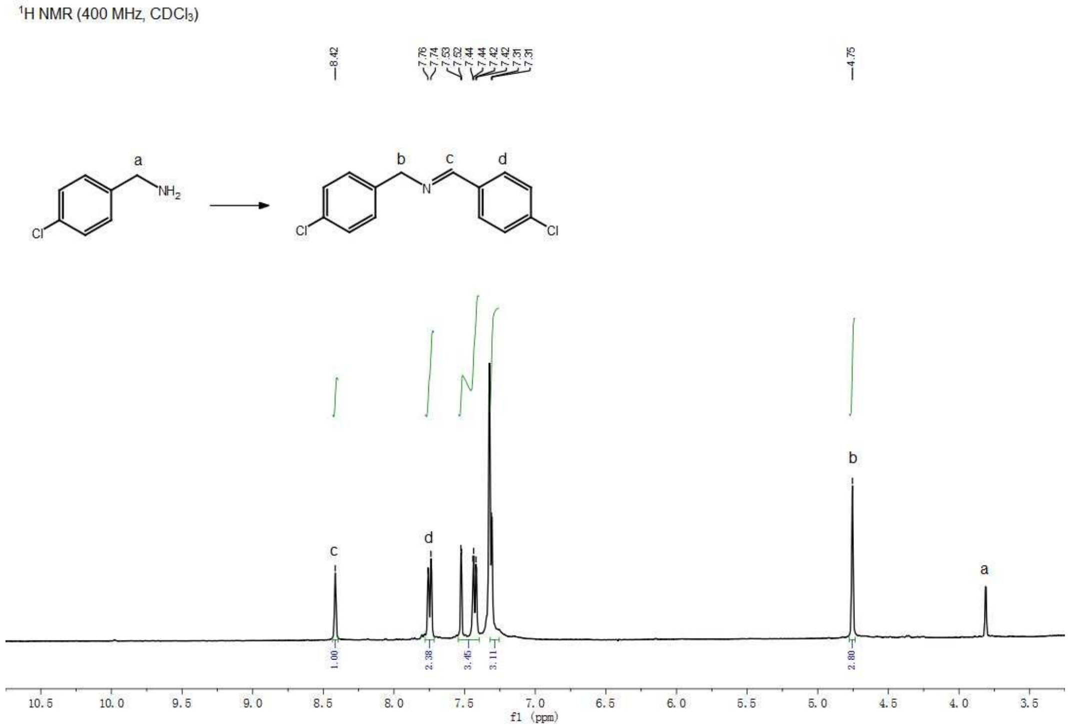


Figure S28b. ^{1}H NMR spectrum of the reaction product using 4-chlorobenzylamine as substrate in Table 2.

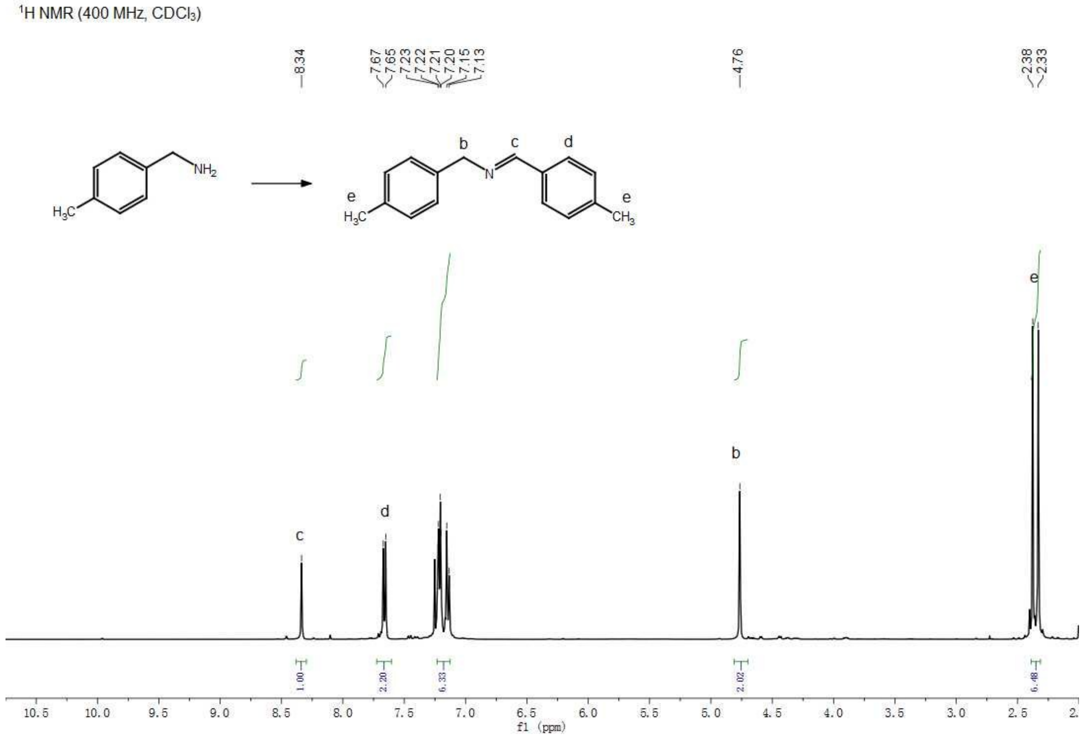


Figure S28c. ^{1}H NMR spectrum of the reaction product using 4-methylbenzylamine as substrate in Table 2.

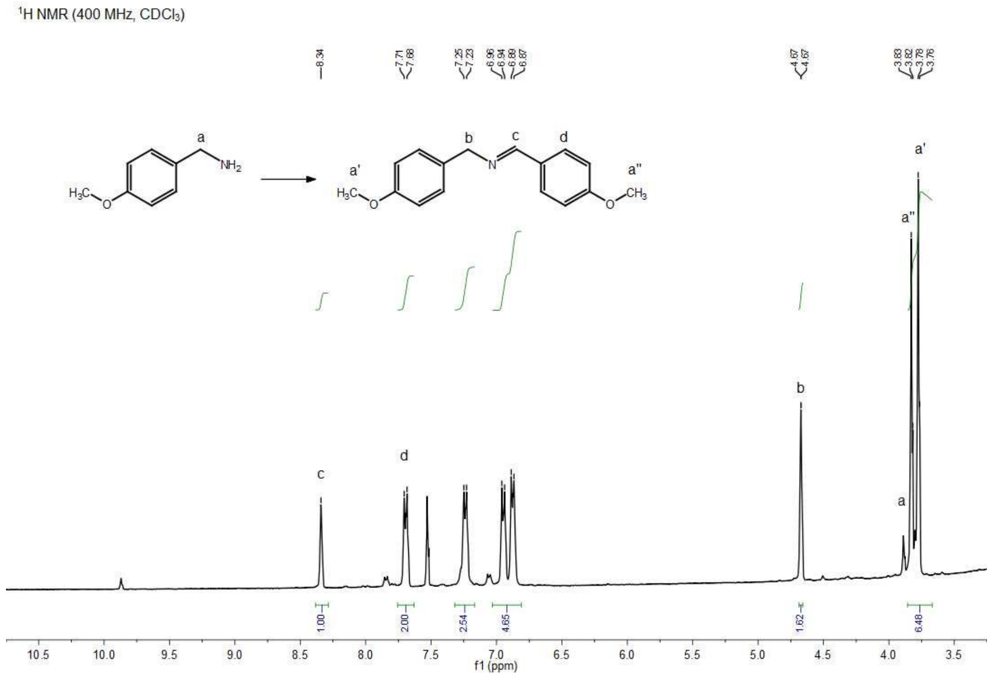


Figure S28d. ^{1}H NMR spectrum of the reaction product using 4-methoxybenzylamine as substrate in Table 2.

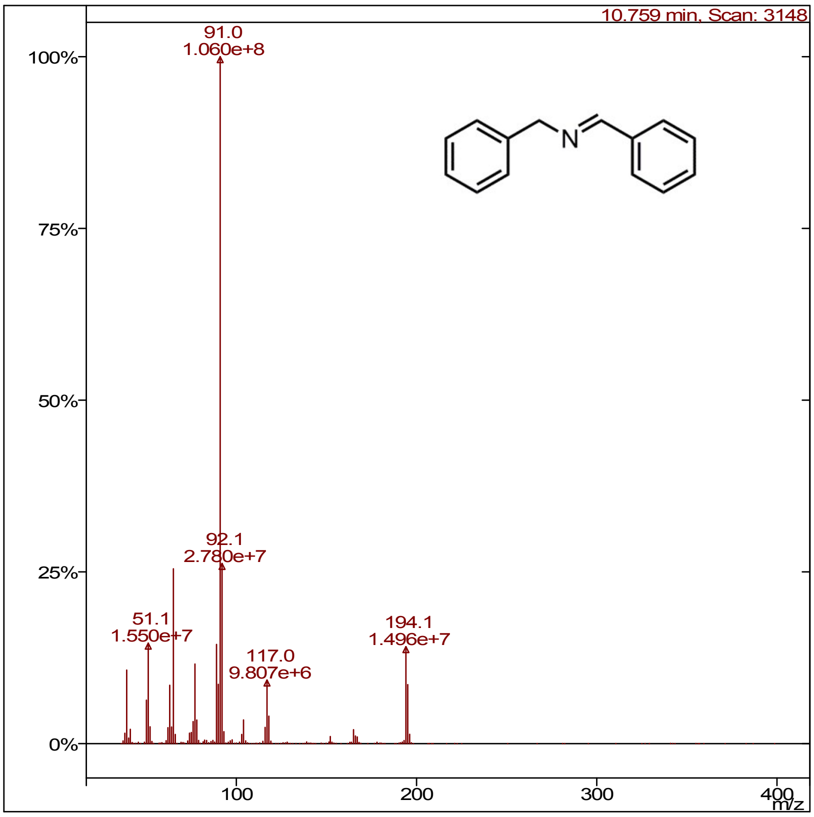


Figure S29a. Mass spectrum of the reaction product in Table 2.

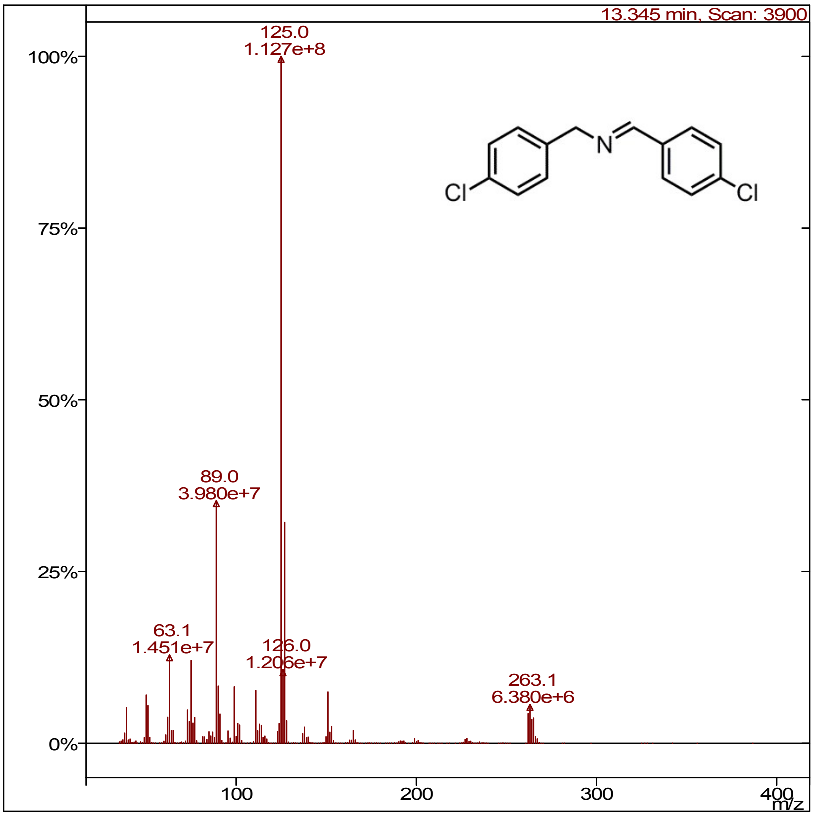


Figure S29b. Mass spectrum of the reaction product in Table 2.

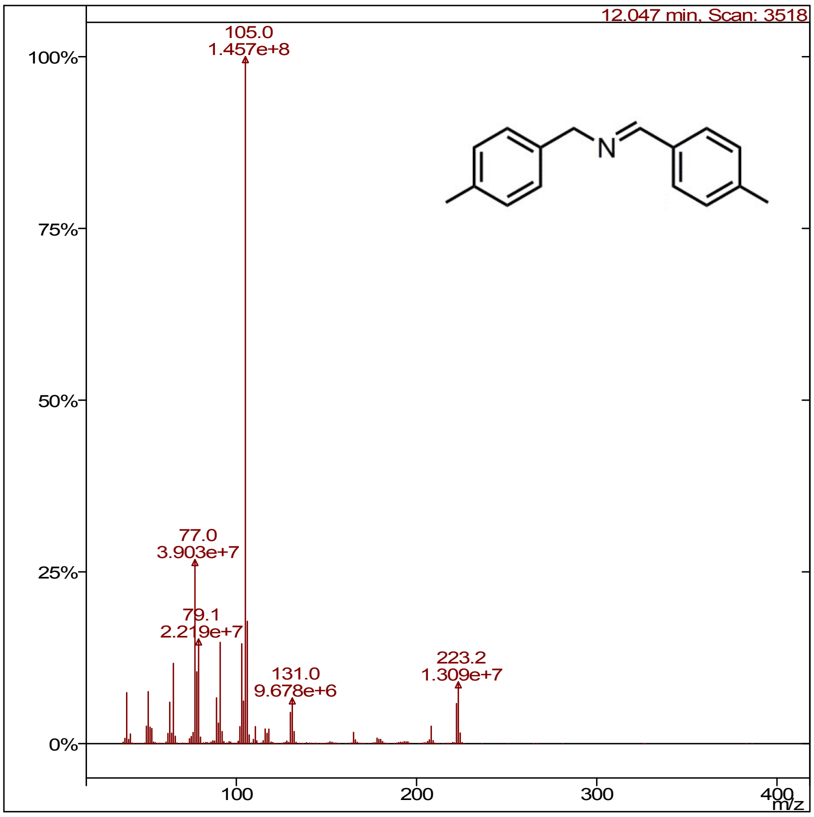


Figure S29c. Mass spectrum of the reaction product in Table 2.

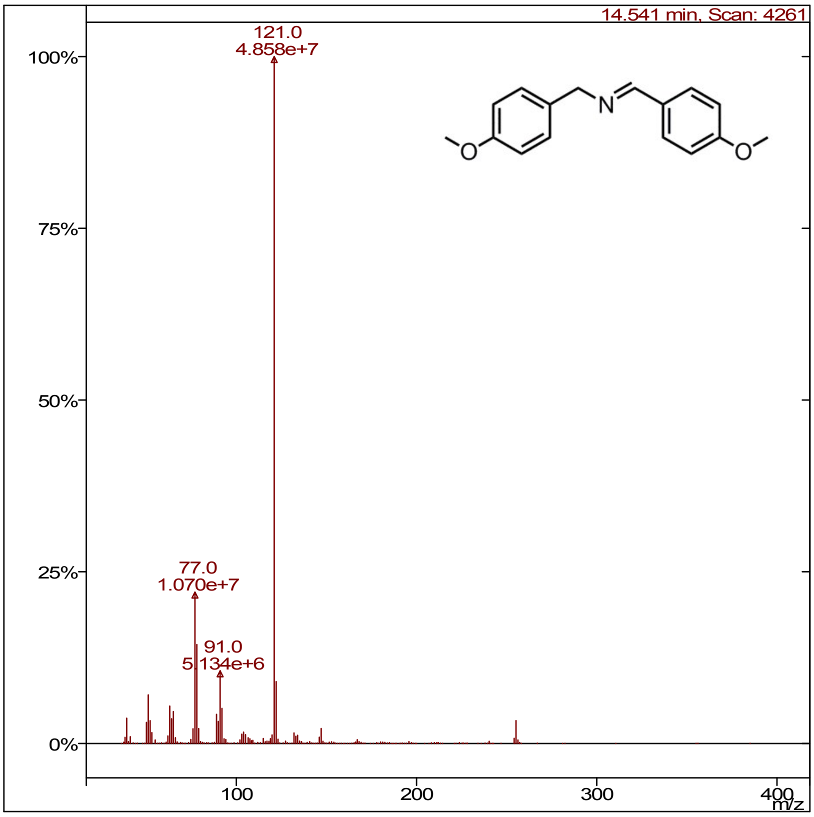


Figure S29d. Mass spectrum of the reaction product in Table 2.

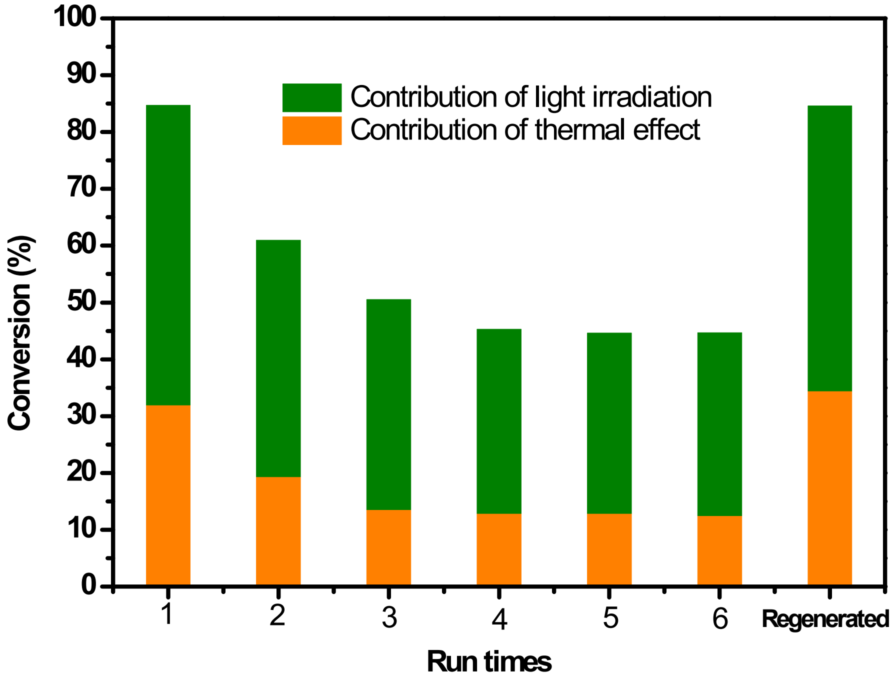


Figure S30. Repeating experiment of photocatalytic oxidative coupling of benzylamine using PANI-ES as catalyst.