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Electronic Supplementary Information

Merging the Catechol-TiO_2 Complex Photocatalysis with TEMPO for Selective Aerobic Oxidation of Amines into Imines

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Table of contents

Reagents and solvents

All the reagents were obtained from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J&K Scientific, etc. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co., LTD. Benzyl-α,α-d2-amine was supplied by CDN Isotopes, Quebec, Canada. Anatase TiO_2 (Ishihara ST-01) used in this paper was purchased from Ishihara Sangyo Kaisha, LTD., Japan. All the reagents and solvents were directly used without further purification.

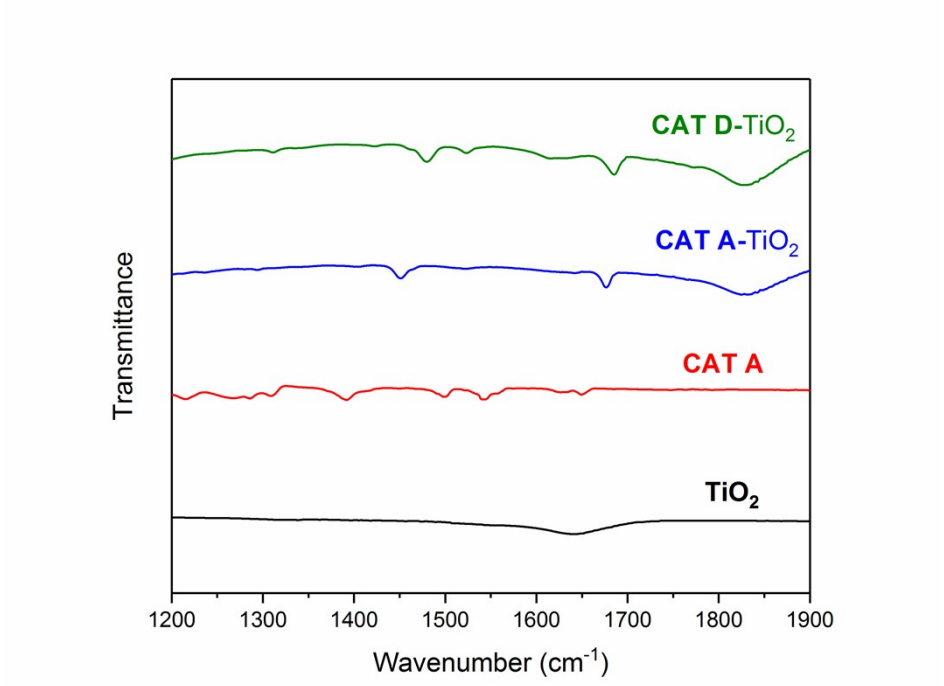

Figure S1. ATR-FTIR spectra of TiO_2, **CAT A**, **CAT A**-TiO_2 and **CAT D**-TiO_2

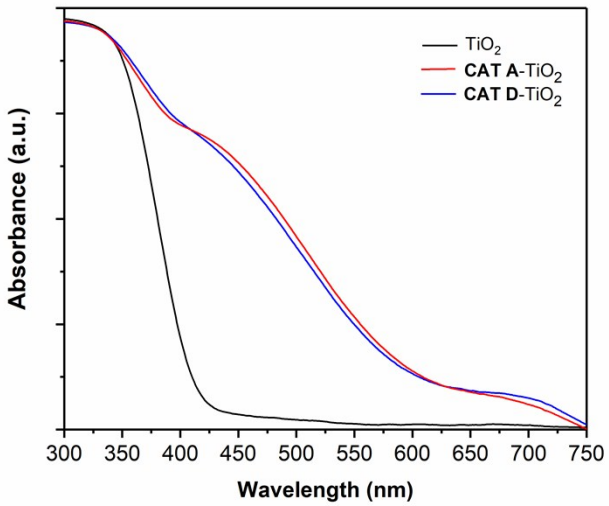

Figure S2. Diffuse reflectance UV-visible spectroscopy of TiO_2, **CAT A**-TiO_2 and **CAT D**-TiO_2

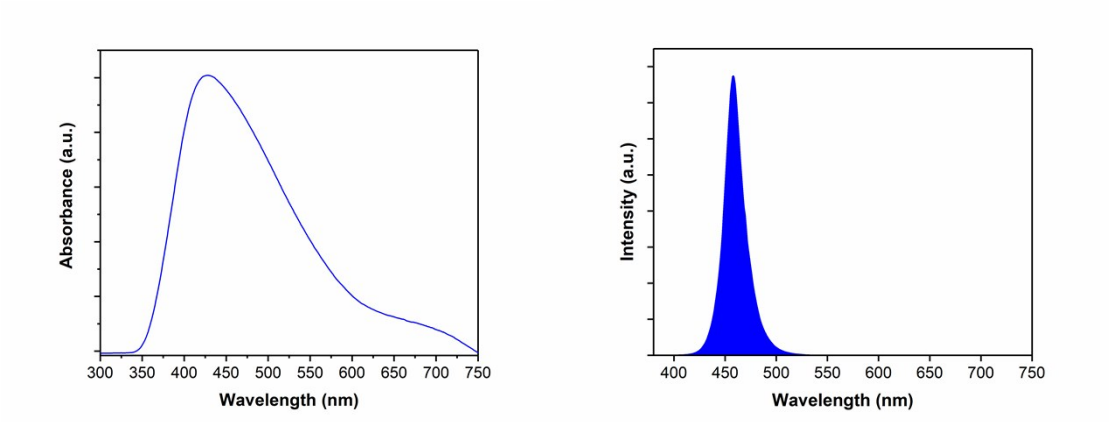

Figure S3. The correlation between photocatalyst and light sources, (a) the UV-visible light absorbance of CAT D-TiO_2; (b) the relative spectrum distribution of blue LED

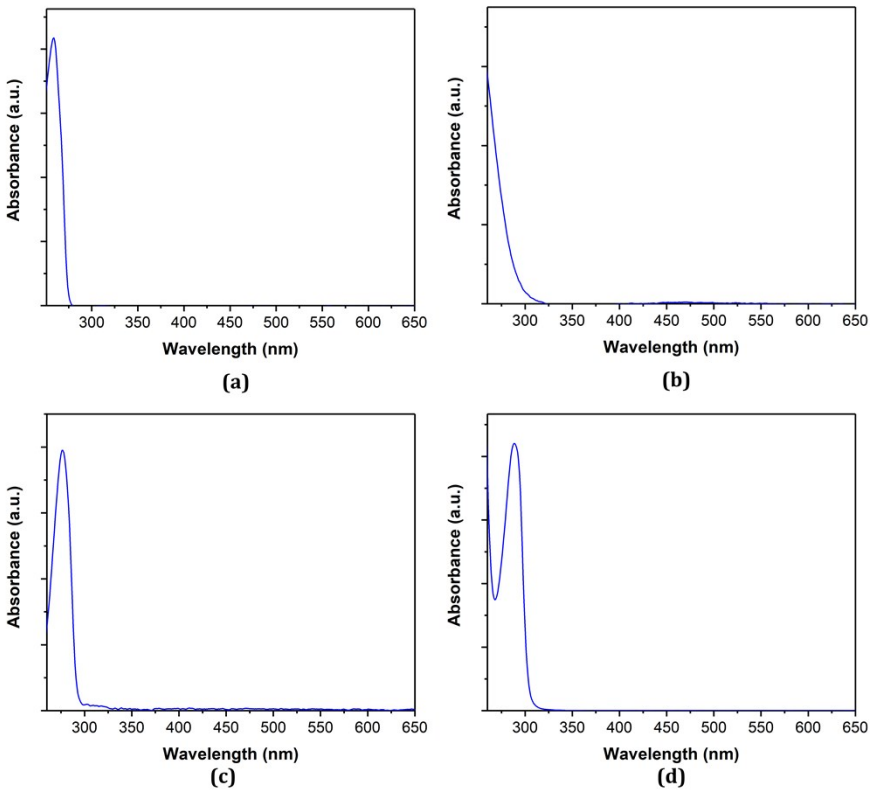

Figure S4. UV-visible absorbance of spectroscopy of benzylamine (a), TEMPO (b), **CAT A** (c) and **CAT D** (d)

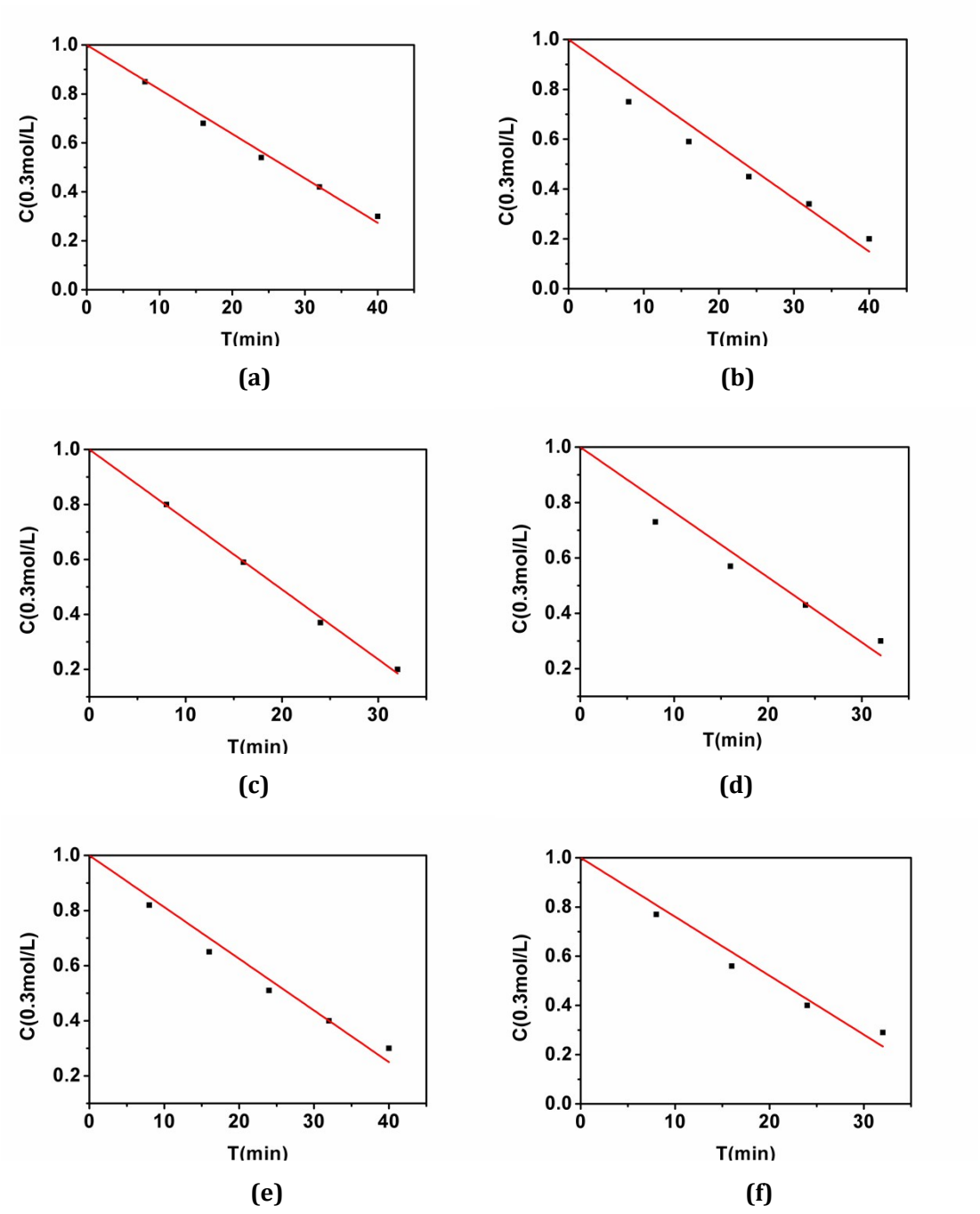

Figure S5. The reaction kinetics profiles for the visible light photocatalytic oxidation of 4-substituted benzylamines. a, H; b, CH_3; c, OCH_3; d, Cl; e, F; f, Br. Reaction conditions: 0.3 mmol of amine, 50 mg TiO_2, 2.4×10^{-3} mmol of **CAT D**, 0.015 mmol of TEMPO, 1 mL of CH_3CN, 3 W blue LED irradiation.

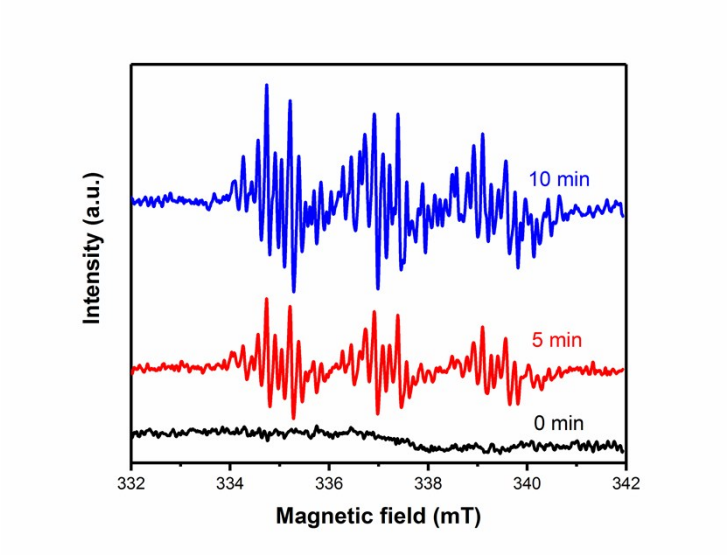

Figure S6. The ESR signals of N-radical captured by PBN during **CAT D**-TiO_2 photocatalysis

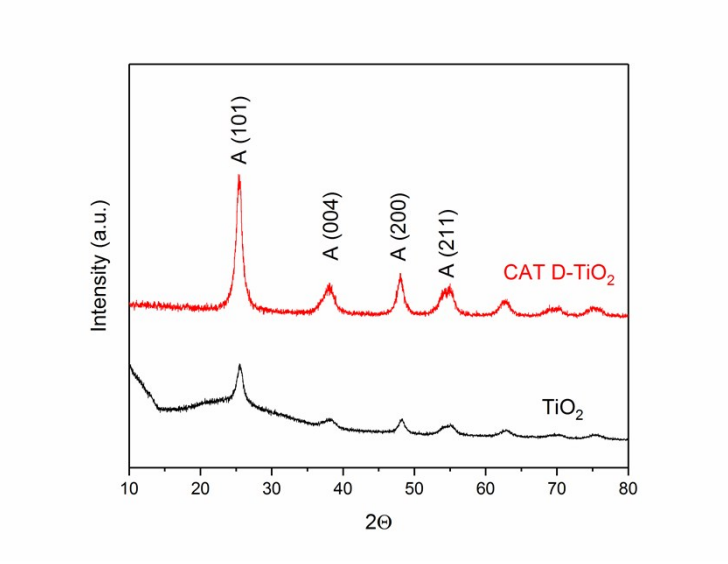

Figure S7. The XRD patterns of anatase TiO_2 and **CAT D**-TiO_2

Table S1. The influence of different LED_S on the selective aerobic oxidation benzylamine to imine under visible light irradiation[a]

Entry	LED	λ_{max} [nm]	Conv.[%][b]	Sel.[%][b]
1	Red	630	0	0
2	Yellow	590	3	98
3	Green	510	16	96
4	Blue	460	68	98
5	Violet	400	85	98
6	White	Continuous	26	98
7	Warm	Continuous	12	97

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO_2, 0.015 mmol of TEMPO, 3 W LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S2. Control experiments for the photocatalytic selective oxidation of benzylamine to imine under visible light irradiation [a]

Entry	Conditions	Conv.[%][b]	Sel.[%][b]
1	Standard	68	98
2	TiO_2	9	96
3	TiO_2, TEMPO	10	97
4	TEMPO	0	0
5	**CAT D**, TEMPO	0	0
6	**CAT D**	0	0
7	Blank	0	0
8	Dark	0	0
9	N_2	6	98
10	CD_3CN	70	94
11	*p*-BQ (0.2 equiv.)	2	98
12	$AgNO_3$ (1 equiv.)	21	72

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO_2, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S3. The influence of initial O_2 pressure on the selective aerobic oxidation benzylamine to imine under visible light irradiation [a]

Entry	Initial O_2 pressure [atm]	Conv.[%]	Sel.[%]
1	0.2	68	98
2	0.5	73	98
3	1.0	76	99
4	1.5	77	97
5	2.0	81	98
6	2.5	81	99

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO_2, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S4. The influence of the solvent on the selective aerobic oxidation benzylamine to imine under visible light irradiation [a]

Entry	Solvent	Conv.[%][b]	Sel.[%][b]
1	CH_3CN	68	98
2	BTF	63	98
3	EtOAc	46	98
4	PhMe	62	98
5	DCM	54	98
6	1,4-Dioxane	53	98

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO_2, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine. BTF, benzotrifluoride; EtOAc, ethyl acetate; PhMe, toluene; DCM, dichloromethane.

Table S5. The influence of the amount of TiO_2 on the selective aerobic oxidation benzylamine to imine under visible light irradiation [a]

Entry	TiO_2 [mg]	Conv.[%][b]	Sel.[%][b]
1	10	35	97
2	20	48	95
3	30	56	98
4	40	61	98
5	50	68	98
6	60	75	98

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S6. The influence of the amount of TEMPO on the selective aerobic oxidation benzylamine to imine under visible light irradiation [a]

Entry	TEMPO [μmol]	Conv.[%][b]	Sel.[%][b]
1	0	18	94
2	3	40	95
3	6	53	98
4	9	62	96
5	12	66	97
6	15	68	98
7	18	68	98
8	21	72	96
9	24	75	98
10	27	76	98
11	30	77	97

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO_2, 3 W blue LED irradiation, 1 mL of CH_3CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.