Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Visible-Light-Driven Self-Coupling and Oxidative Dehydrogenation of Amines to Imines via a Mn(II)-Based Coordination Polymer

Hui Liu,[a] Zhifen Guo,[a] Hui Lv,[a] Xin Liu,[a] Yan Che,[a] Yingchun Mei,[b] Rong Bai,[a] Yanhong Chi[a] and Hongzhu Xing*[a]

[a]Provincial Key Laboratory of Advanced Energy Materials, College of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, China.

[b]Dyestuff Factory, Jilin Petrochemical Company, 19 Zunyi East Road, Jilin 132022, China.

E-mail: xinghz223@nenu.edu.cn

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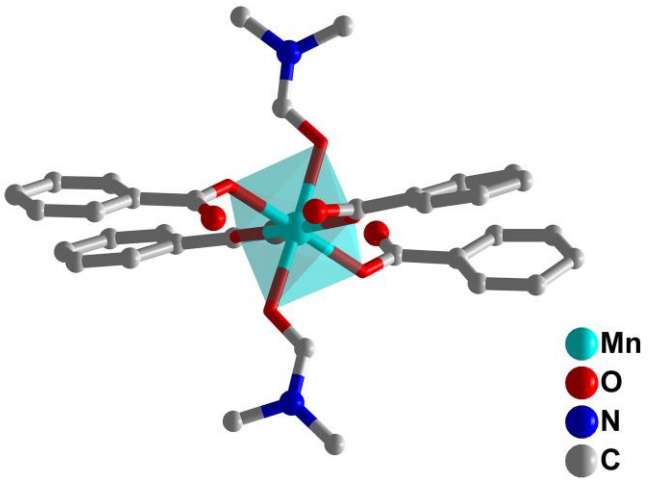


Fig. S1 Coordination environments of Mn(II) ion (H atoms are omitted for clarity).

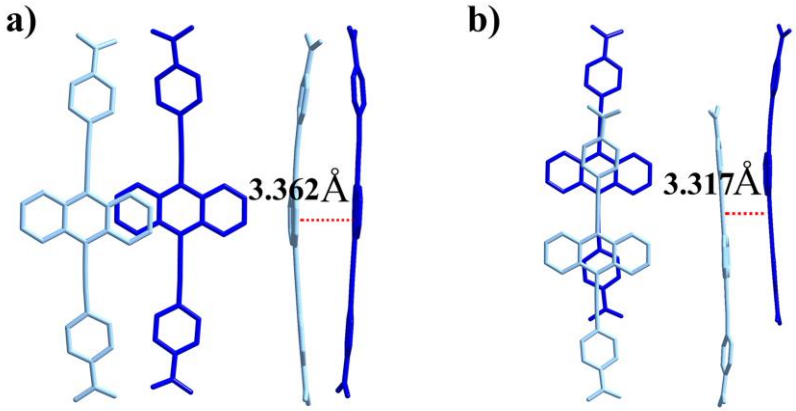


Fig. S2 Stacking interaction between organic linker ADBEB: (a) intrachain π-π interaction; (b) interchain π-π interaction.

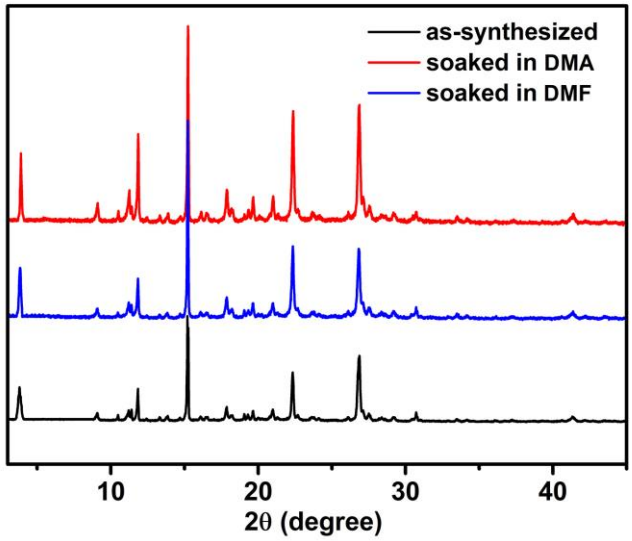


Fig. S3 PXRD patterns of **1** soaking in DMA and DMF for one day.

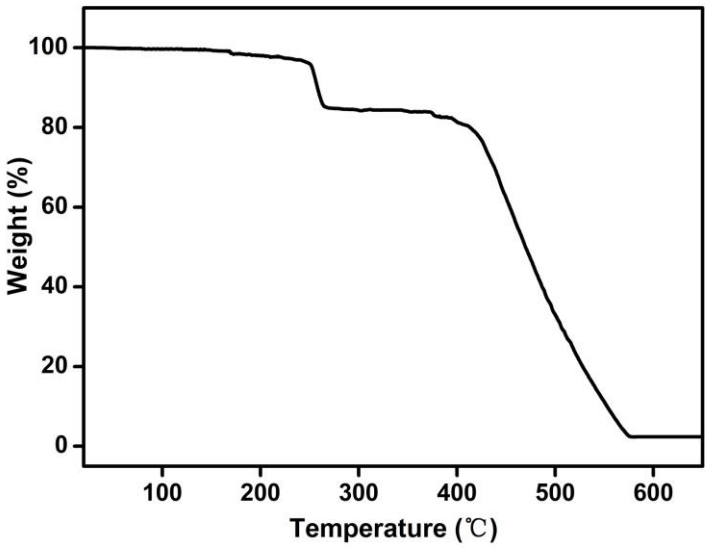


Fig. S4 TG curve of **1**.

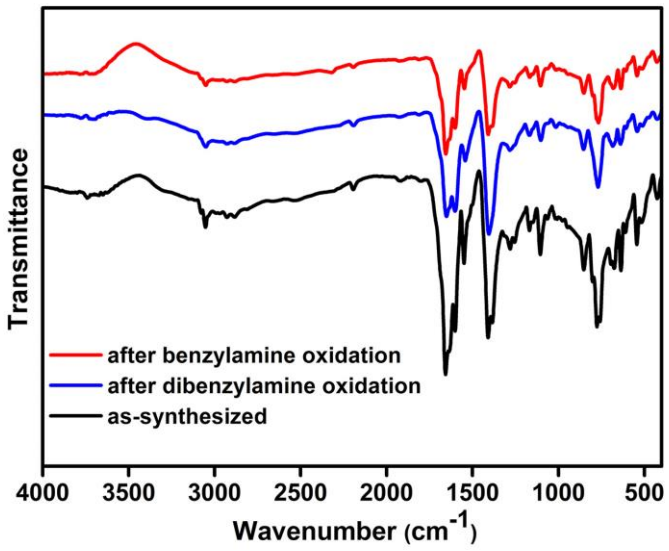


Fig. S5 FTIR spectra of **1** before and after photocatalytic oxidation.

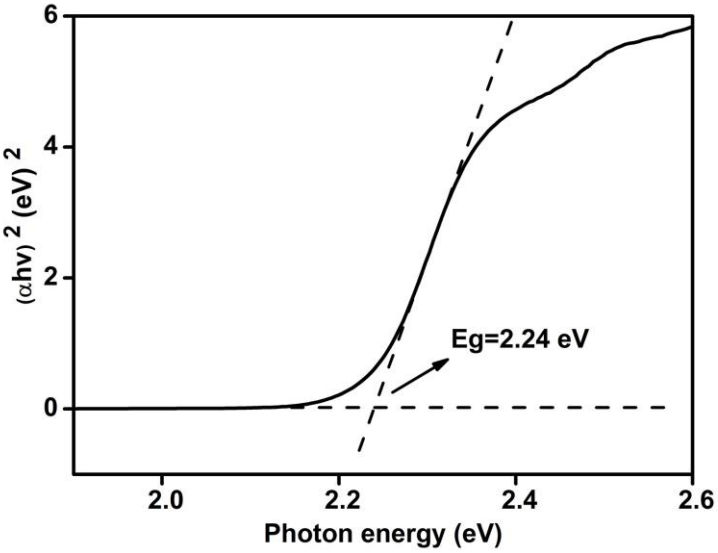


Fig. S6 Tauc plot of **1**.

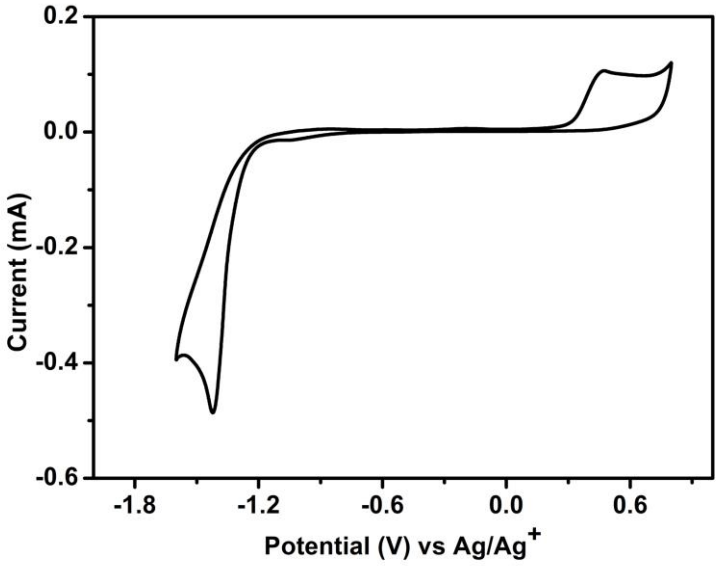


Fig. S7 Cyclic voltammetry curve of **1** in acetonitrile.

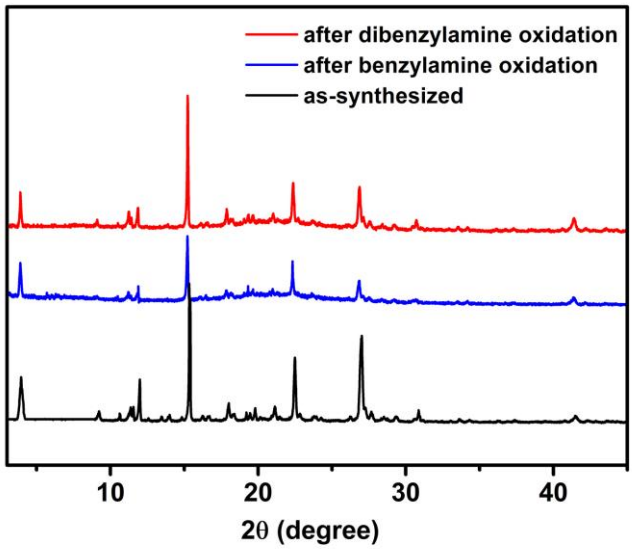


Fig. S8 PXRD patterns of **1** after photocatalytic oxidation.

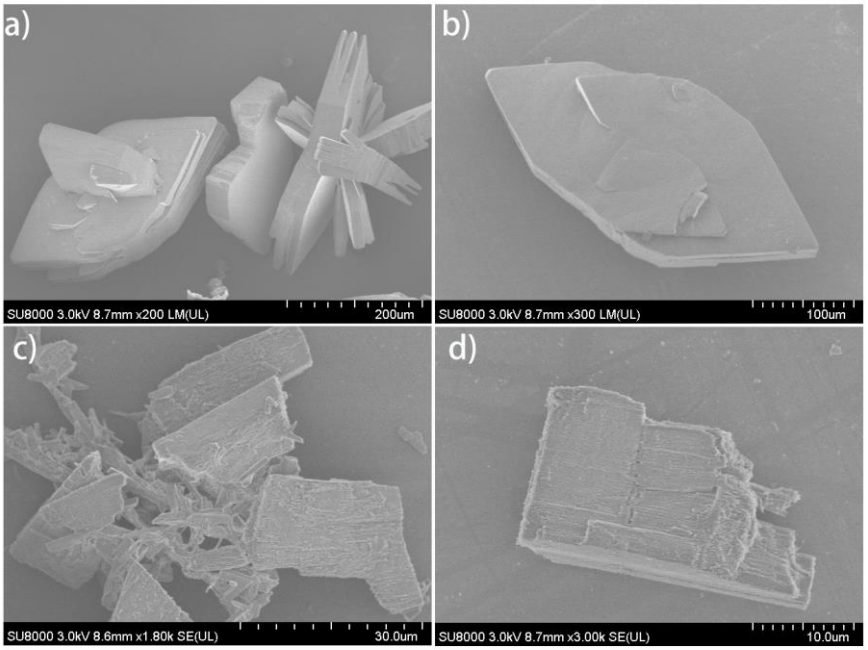


Fig. S9 SEM images of **1**. (a, b) as-synthesized; (c, d) after photocatalytic oxidization of benzylamine (c) and dibenzylamine (d).

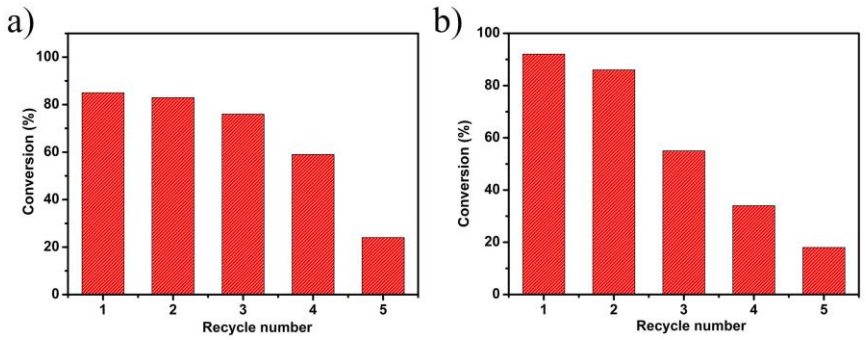


Fig. S10 Cycling experiments using ADBEB as photocatalyst for benzylamine (a) and dibenzylamine (b) conversion. The experiments were carried out by consecutively adding equivalent of substrate in the system.

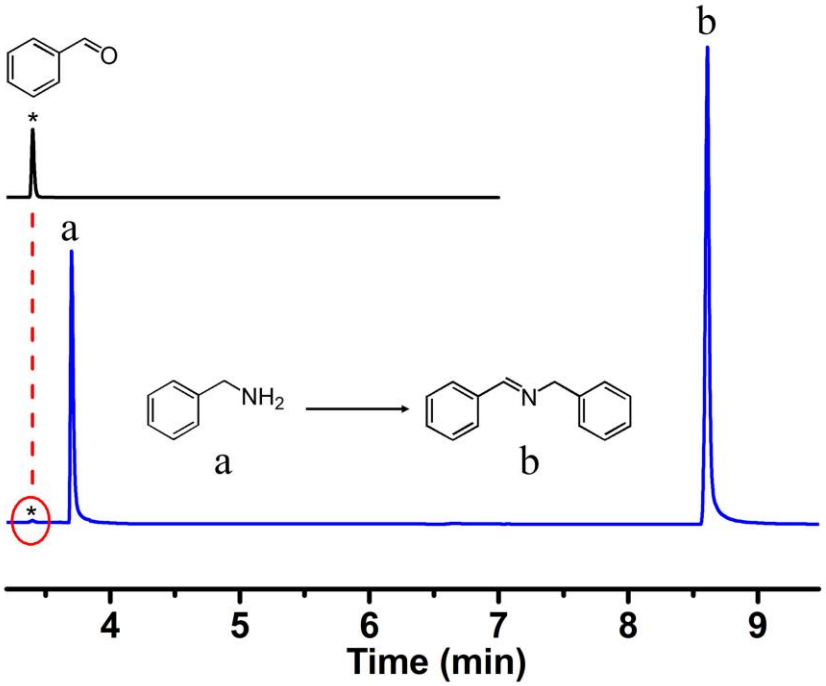


Fig. S11 The detection of benzaldehyde by GC after 25 minutes reaction.

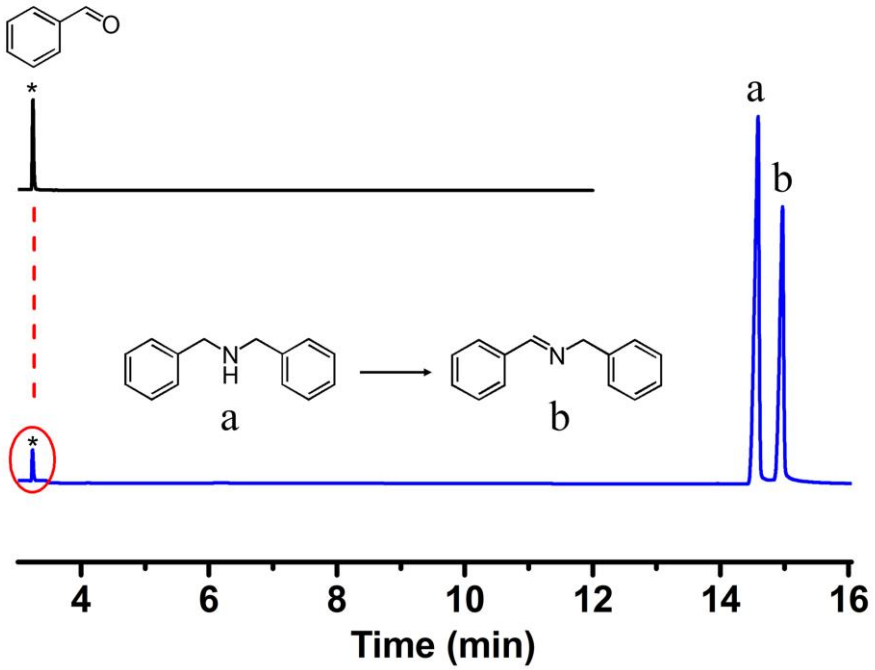


Fig. S12 The detection of benzaldehyde by GC after 60 minutes reaction.

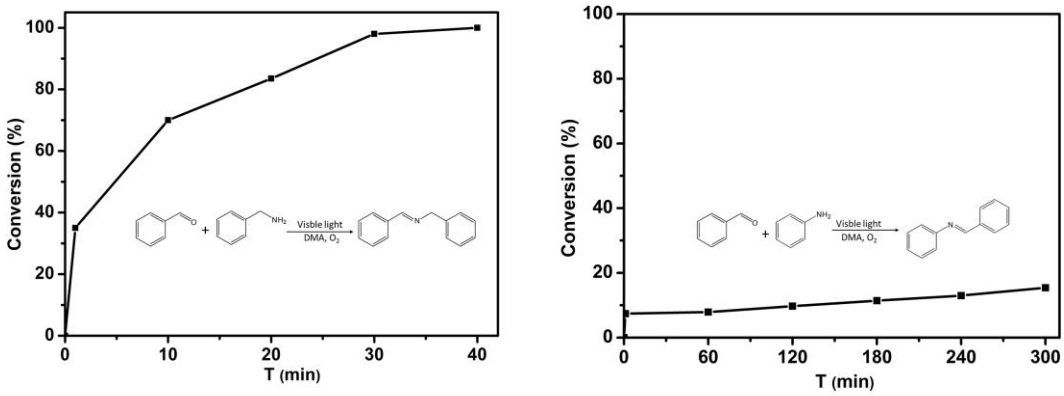


Fig. S13 Reactions of benzaldehyde with benzylamine (left) and aniline (right). Reaction conditions: 0.2 mmol benzaldehyde and 0.2 mmol amine in 1 ml DMA under oxygen atmosphere.

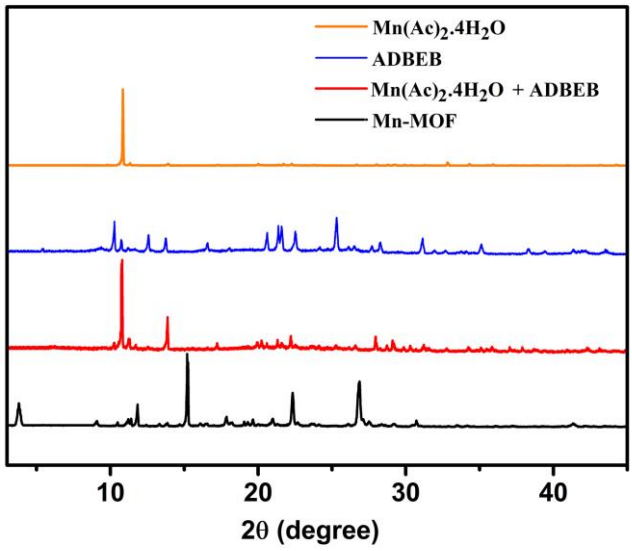
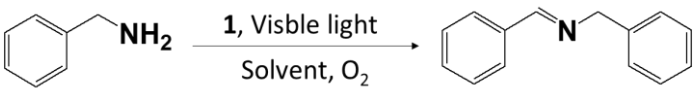


Fig. S14 PXRD patterns of the precursors. The red curve is the pattern for the mixture of metal salt and ADBEB which was mechanically grinded for half an hour.

Table S1 Crystal data and structural refinement of **1**.

Compound	**1**
empirical formula	$MnC_{70}H_{46}N_2O_{10}$
formula weight	1130.03
space group	$Pca2_1$
crystal system	Orthorhombic
a / Å	18.0175(4)
b / Å	23.2759(6)
c / Å	13.0686(3)
α / °	90
β / °	90
γ / °	90
V / Å^3	5480.6(2)
Z	4
F (000)	2340
θ range collected	3.102 to 62.449
limiting indices	$-20 \le h \le 20$ $-26 \le k \le 26$ $-15 \le l \le 15$
Reflections collected / unique	23478 / 8728
data / restraints / parameters	8728 / 1 / 753
R (int)	0.0550
goodness-of-fit on F^2	1.048
Final R indices ($[I > 2\sigma(I)]$)	$R_1 = 0.0373$, $wR_2 = 0.0867$
R indices (all data)	$R_1 = 0.0459$, $wR_2 = 0.\ 0.0904$

Table S2 Solvent influence on the photocatalytic self-coupling of benzylamine.[a]



Entry	Solvent	*t* [min]	Conv. [%][b]	Sel. [%][b]
1	DMF	80	99	99
2	DMA	120	99	98
3	CH_3CN	180	95	99
4	$CH_3COOC_2H_5$	180	80	85
5	CH_3OH	180	70	99
6	1,4-dioxane	180	54	99
7	$CHCl_3$	180	46	99
8	DMF/DMA(1/1)	50	99	99
9	DMF/DMA(4/1)	65	99	99
10	DMF/DMA(1/4)	75	99	99

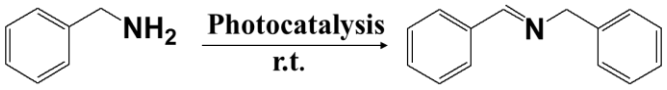
[a]Reaction conditions: 0.2 mmol amine, 6 mg **1**, O_2 atmosphere, visible light, 1 ml solvent. [b]Determined by GC analysis.

Table S3 Photocatalytic self-coupling of benzylamine under various conditions.[a]

Entry	Variable	Conv. [%][b]	Sel. [%][b]
1	None	99	99
2	No **1**	-	-
3	No light	-	-
4	N_2 atmosphere	2	99
5	air atmosphere	45	99
6	ADBEB	85	92
7	$Mn(Ac)_2{\cdot}4H_2O$	-	-
8	$Mn(Ac)_2{\cdot}4H_2O$ + ADBEB	24	90

[a]Reaction conditions: 0.2 mmol amine, 6 mg **1**, O_2 atmosphere, visible light, 1 ml DMF/DMA, reaction time of 50 min. [b]Determined by GC analysis.

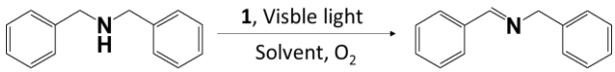
Table S4 Performances of visible-light-driven self-coupling of benzylamine using various MOF photocatalysts.



Entry	Catalyst	T [K]	*t* [h]	Conv. [%]	TOF [h^{-1}][a]	Refs
1	RPF-31-Nd	r.t.	18	60	0.33	1
2	RPF-31-Sm	r.t.	18	65	0.36	1
3	RPF-31-La	r.t.	18	71	0.39	1
4	RPF-32-Ho	r.t.	18	74	0.41	1
5	RPF-30-Er	r.t.	18	76	0.42	1
6	NH_2-MIL-125(Ti)	r.t.	12	73	5.3	2
7	NNU-45	r.t.	2.5	99	13.4	3
8	Zn-PDI	r.t.	4	74	18.5	4
9	**1**	r.t.	1	99	24	this work
10	PCN-222	r.t.	1	100	25.7	5

[a]TOFs (turnover number frequency) were calculated as (mmol product / (mmol catalyst × reaction time).

Table S5 Solvent influence on photocatalytic dehydrogenation of dibenzylamine.[a]



Entry	Solvent	Conv. [%][b]	Sel. [%][b]
1	DMA	99	99
2	CH_3OH	65	98
3	CH_3CH_2OH	50	99
4	$CH_3COOC_2H_5$	47	99
5	1,4-dioxane	40	99
6	DMF	35	99
7	$CHCl_3$	19	99
8	DMF/DMA(1/1)	88	99
9	CH_3OH /DMA(1/1)	82	98
10	CH_3CH_2OH /DMA(1/1)	83	98

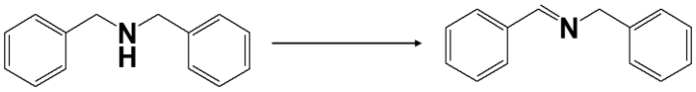
[a]Reaction conditions: 0.2 mmol amine, 6 mg **1**, O_2 atmosphere, visible light, 1 ml solvent, reaction time of 120 min. [b]Determined by GC analysis.

Table S6 Photocatalytic dehydrogenation of dibenzylamine under various conditions.[a]

Entry	Variable	Conv. [%][b]	Sel. [%][b]
1	None	99	99
2	No **1**	-	-
3	No light	-	-
4	N_2 atmosphere	3	99
5	air atmosphere	41	99
6	ADBEB	92	91
7	$Mn(Ac)_2{\cdot}4H_2O$	-	-
8	$Mn(Ac)_2{\cdot}4H_2O$ + ADBEB	34	90

[a]Reaction conditions: 0.2 mmol amine, 6 mg **1**, O_2 atmosphere, visible light, 1 ml DMA, reaction time of 120 min. [b]Determined by GC analysis.

Table S7 Performances of oxidative dehydrogenation of dibenzylamine using different catalysts under visible light or heating condition.



Entry	Catalyst	Visible light	T [K]	*t* [h]	Conv. [%]	Sel. [%]	TOF [a] [h^{-1}]	Refs
1	TiO_2	Y	r.t.	8	81	45	0.017	6
2	Nb_2O_5	Y	r.t.	20	97	71	0.84	7
3	$ZnIn_2S_4$	Y	r.t.	0.75	77	83	2.7	8
4	NH_2-MIL-125(Ti)	Y	r.t.	12	68	78	4.9	2
5	Phenothiazine Dyes	Y	r.t.	20	100	95	10	9
6	**1**	Y	r.t.	2	99	99	10	this work
7	$[Ru^{II}(TDCPP)(CO)]$	Y	r.t.	8	99	99	12.5	10
8	PCN-222	Y	r.t.	1	100	100	25.7	5
9	NHPI/Fe(BTC)	N	373	24	12	100	0.04	11
10	Bulk $Cu_3(BTC)_2$	N	313	3	17	15	0.8	12
11	$Cu_3(BTC)_2$-A	N	313	3	27	24	1.3	12
12	$Cu_3(BTC)_2$-B	N	313	3	53	41	2.5	12
13	MOF-253	N	373	15	90	99	4	13

[a]TOFs (turnover number frequency) were calculated as (mmol product / (mmol catalyst × reaction time)).

Table S8 Effect of different quenchers on the photocatalytic self-coupling and dehydrogenation of amines.[a]

Entry	Substrate	Quencher (equiv to amine)	*t* [min]	Conv. [%][b]
1	benzylamine	-	50	99
2	benzylamine	TEMP (1.0)	50	40
3	benzylamine	TEMP (10)	50	12
4	benzylamine	DMPO (1.0)	50	58
5	benzylamine	DMPO (10)	50	16
6	benzylamine	TEMP (10) DMPO (10)	50	3
7[e]	benzylamine	TEOA (1.0)	50	32
8	dibenzylamine	-	120	99
9	dibenzylamine	TEMP (1.0)	120	35
10[c]	dibenzylamine	TEMP (10)	120	5
11	dibenzylamine	DMPO (1.0)	120	32
12	dibenzylamine	DMPO (10)	120	7
13	dibenzylamine	TEMP (10) DMPO (10)	120	2
14[e]	dibenzylamine	TEOA (1.0)	120	62

[a]Reaction conditions: 0.2 mmol amine, 6 mg **1**, O_2 atmosphere, visible light, 1 mL Solvent. [b]Determined by GC analysis. TEMP was added as scavenger for singlet oxygen; DMPO was added as scavenger for superoxide radical; TEOA was added as scavenger for hole.

Table S9 Effects of other scavengers on the conversion of benzylamine and dibenzylamine.[a]

Reactive species	Quenchers	Conversion for benzylamine	Conversion for dibenzylamine
Superoxide radical	Benzoquinone (BQ)	40%	25%
hole	Triethylamine (TEA)	70%	68%
electron	$Ag(NO_3)$	45%	35%
Hydroxyl radical	Isopropanol (IPA)	97%	98%

[a]The quenchers in the reaction is equivalent to amines, and the conversion of the reaction was detected by GC at 50 mins (for benzylamine) and 120 mins (for dibenzylamine).

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