Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A visible-light-responsive metal-organic framework for highly efficient and selective photocatalytic oxidation of amines and reduction of nitroaromatics

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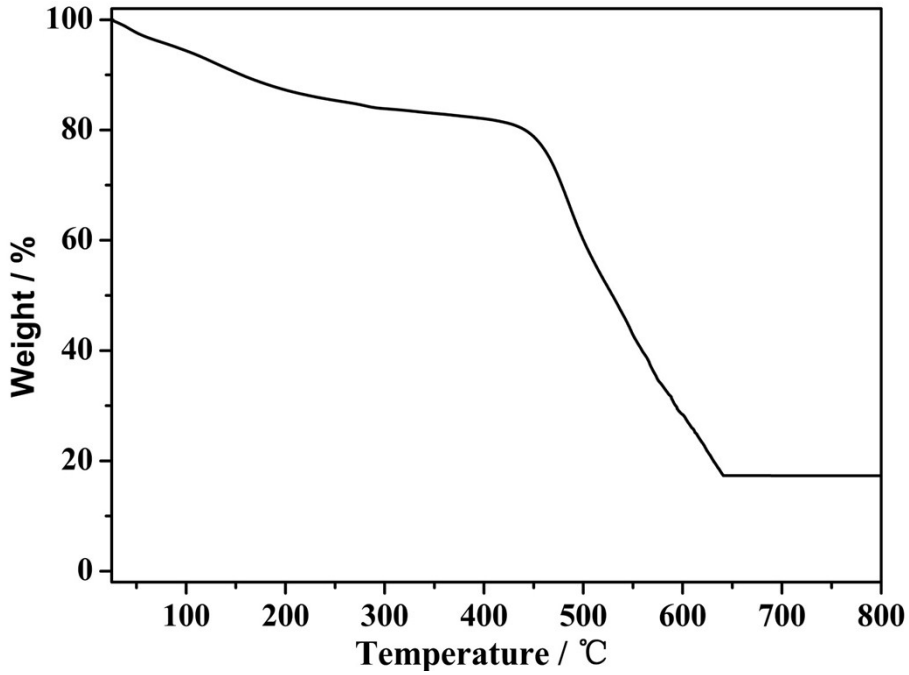


Figure S1. TG curve of **1**.

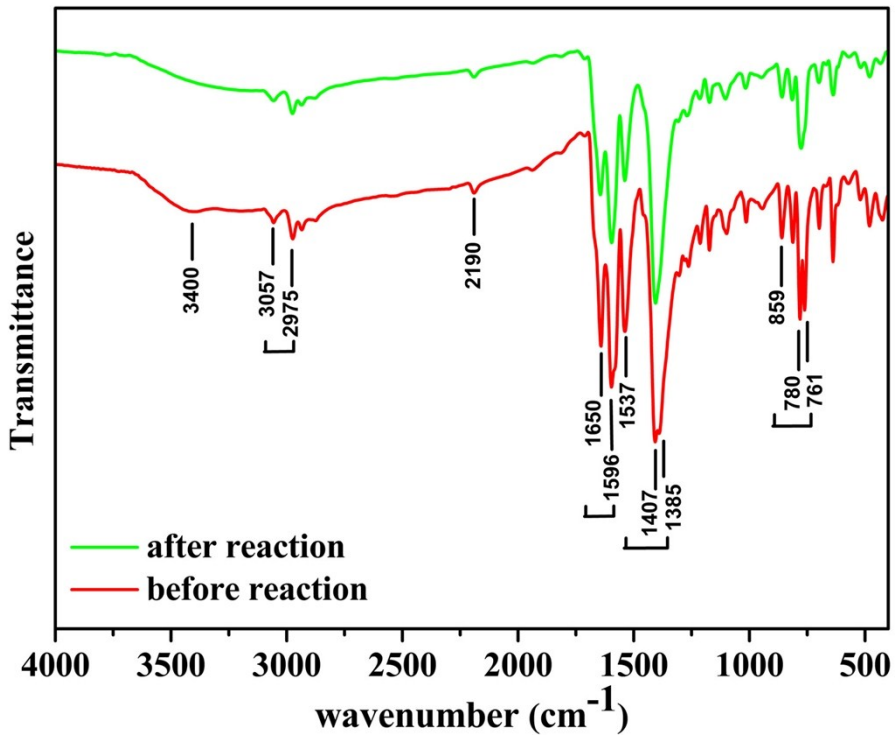


Figure S2. FTIR spectra of **1** before and after reaction.

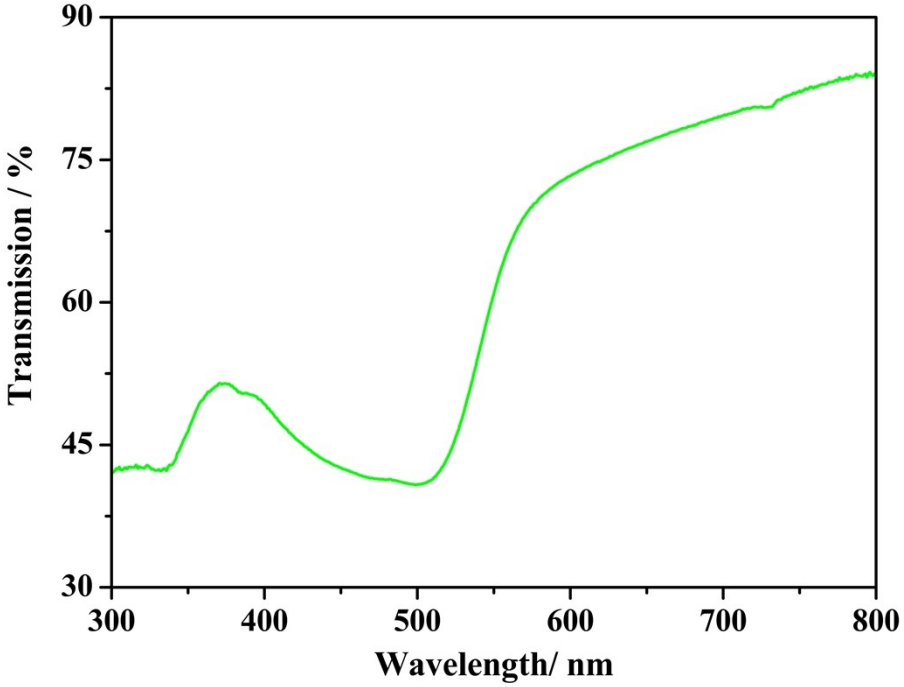


Figure S3. UV-Vis Transmission of **1**

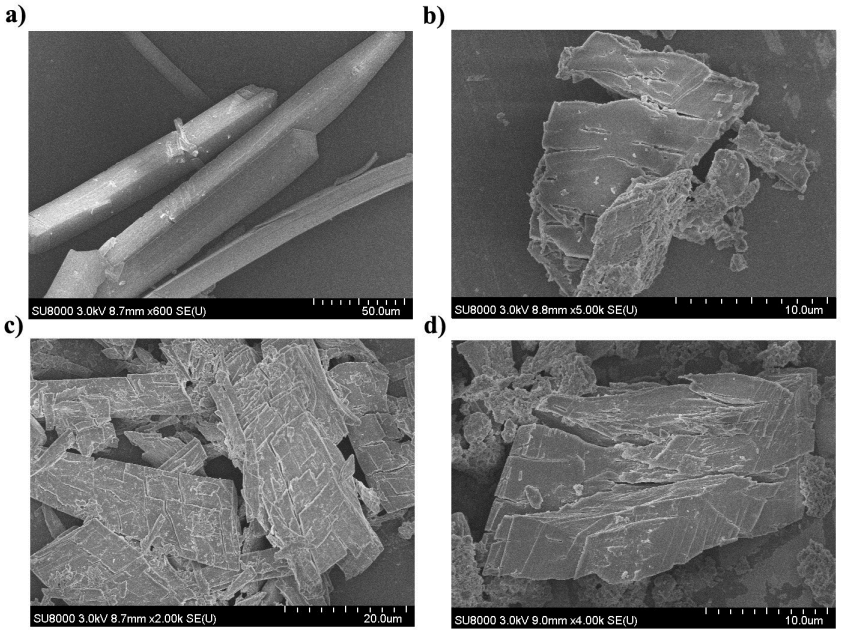


Figure S4. (a) Before reaction. (b) After benzylamine reaction. (c) After dibenzylamine reaction. (d) After nitrobenzene reaction.

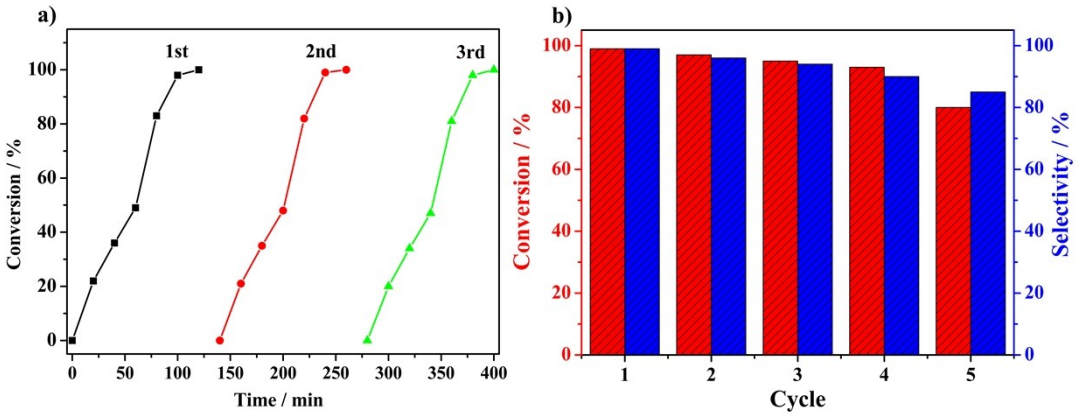


Figure S5. (a) Reaction trace for the dehydrogenation of secondary amines. (b) Conversion and selectivity in different runs.

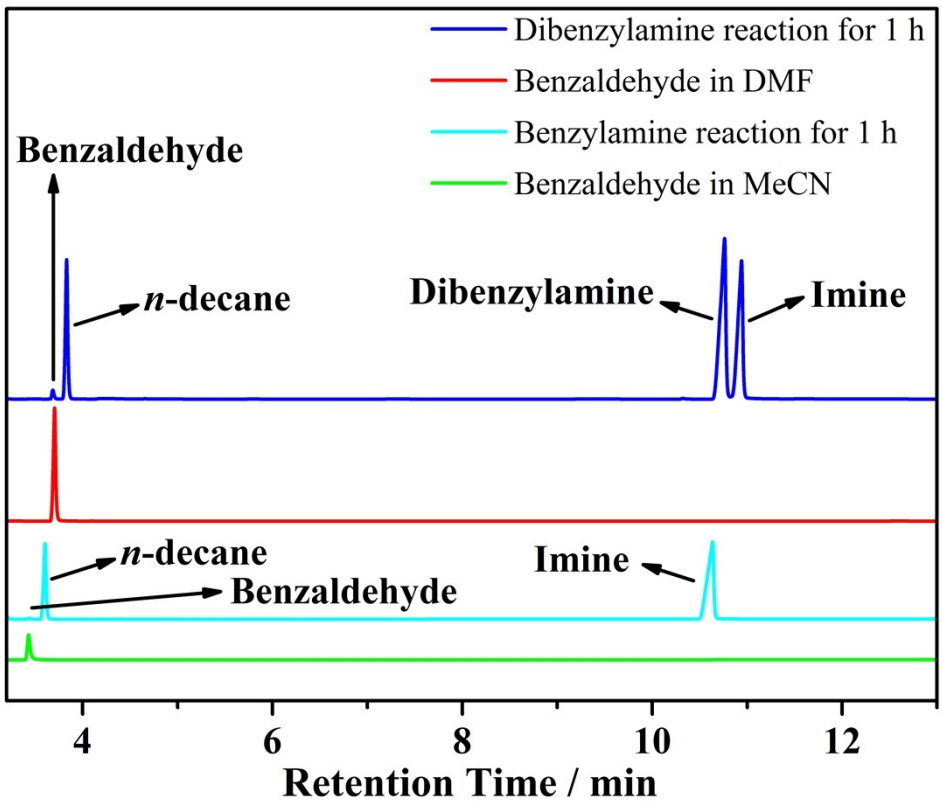


Figure S6. Formation of trace amount of benzaldehyde in the reaction of dibenzylamine and benzylamine at 1 h.

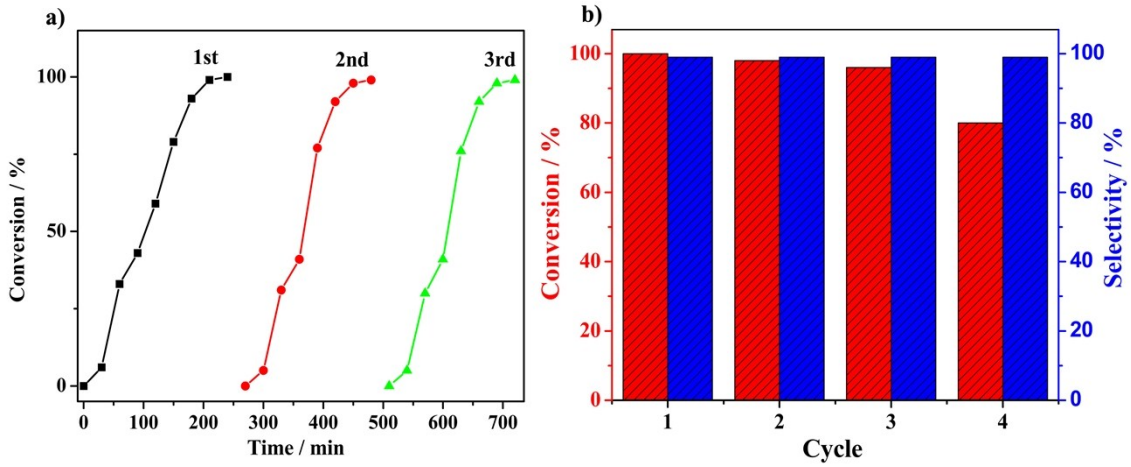
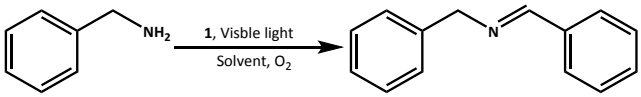


Figure S7. (a) Reaction trance for the photoreduction of nitrobenzene. (b) Conversion and selectivity in different runs.

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

Compound	**1**
empirical formula	$Zn_3C_{64}H_{32}O_{10}$
formula weight	1157.07
crystal system	Monoclinic
space group	*C*2/*m*
a / Å	37.121(3)
b / Å	30.255(3)
c / Å	6.0011(5)
α / degree	90.0000
β / degree	94.396(3)
γ / degree	90.0000
V / Å^3	6720.0(10)
Z	2
F(000)	1172.0
θrange collected / degree	2.54 to 20.66
limiting indices	-36≤*h*≤36 -30≤*k*≤30 -5≤*l*≤5
Reflections collected / unique	7359/2359
data / restraints / parameters	3551/95/200
R (int)	0.0796
goodness-of-fit on F^2	1.041
Final *R* indices ([$I > 2\sigma(I)$])	R_1 = 0.0550 wR_2 = 0.1477
R indices (all data)	R_1 = 0.0867 wR_2 = 0.1675

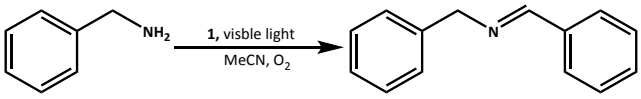
Table S2. Solvent influence on photocatalytic self-coupling of benzylamines over **1.**[a]



Solvent	Time [h]	Yield. [%][b]
MeCN	1	99
DMF	2	99
AcOEt	2	99
DMSO	4	99
EtOH	5	99
MeOH	6	99
$CHCl_3$	6	99

[a]Reaction conditions: 0.2 mmol benzylamines, 5 mg **1**, 1 mL solvent. [b]Determined by GC using *n*-decane as internal standard.

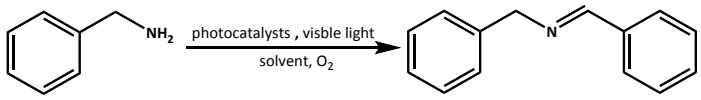
Table S3. Photocatalytic self-coupling of benzylamines under various conditions.[a]



Entry	Photocatalyst	O_2	Light	Conv. [%][b]
1	+	+	+	99
2[c]	+	+	+	24
3	-	+	+	-
4	+	+	-	-
5[d]	+	-	+	25
6[e]	+	-	+	50
7[f]	+	+	+	21
8[g]	+	+	+	37
9[h]	+	+	+	12

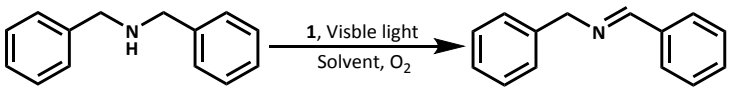
[a]Reaction conditions: 0.2 mmol amine, 5 mg **1**, 1 mL MeCN, 60 min under visible light. [b]Determined by GC using *n*-decane as the internal standard. [c]ADBEB. [d]N_2. [e]Air. [f]TEOA was added a hole scavenge. [g]10 µL TEMP was added as a singlet oxygen scavenge. [h]10 µL DMPO was added as a superoxide radical scavenger.

Table S4. Performances of visible-light-induced self-coupling of benzylamine using MOFs photocatalysts at room temperature.



catalyst	solvent	T [h]	Yield. [%]	TOF [h^{-1}]	Refs
ZJU-56-0.2	CH_3CN	24	62	2.6	1
ZJU-56-0.6	CH_3CN	24	84	3.5	1
NH_2-MIL-125(Ti)	CH_3CN	12	73	5.3	2
In-MOF	DMSO	2.5	99	13.4	3
Zn-PDI	CH_3CN	4	74	18.5	4
PCN-222	CH_3CN	1	100	25.7	5
1	CH_3CN	1	99	45.8	This work

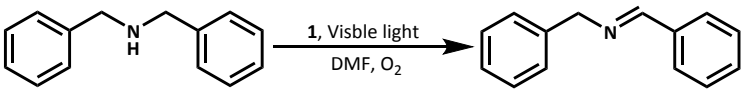
Table S5. Solvent influence on photocatalytic dehydrogenation of dibenzylamine over **1.**[a]



Solvent	Time [h]	Yield. [%][b]
DMF	2	99
DMSO	3	99
EtOH	6	60
$CHCl_3$	6	72
MeOH	6	67
AcOEt	6	57
MeCN	8	99

[a]Reaction conditions: 0.2 mmol secondary amines, 5 mg **1**, 1 mL solvent. [b]Reactions were analysed by GC using *n*-decane as the internal standard.

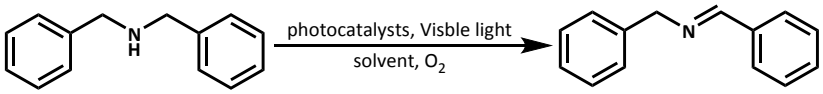
Table S6. Photocatalytic dehydrogenation of dibenzylamine under various conditions.[a]



Entry	Photocatalyst	O_2	Light	yield. [%][b]
1	+	+	+	99
2	-	+	+	-
3	+	+	-	-
4[c]	+	-	+	-
5[d]	+	-	+	30
6[e]	+	+	+	28
7[f]	+	+	+	59
8[g]	+	+	+	48

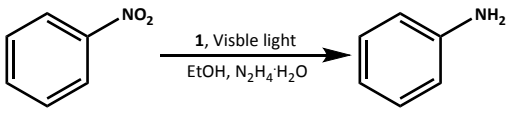
[a]Reaction conditions: 0.2 mmol amine, 5 mg **1**, 1 mL DMF, 2 hours under visible light. [b]Determined by GC using *n*-decane as the internal standard. [c]N_2. [d]Air. [e]TEOA was added a hole scavenge. [f]10 μL TEMP was added as a singlet oxygen scavenge. [g]10 μL DMPO was added as a superoxide radical scavenger.

Table S7. Performances of visible-light-induced dehydrogenation of dibenzylamine using various photocatalysts at room temperature.



Catalyst	Solvent	T [h]	Yield. [%]	TOF [h^{-1}]	Refs
$BiVO_4$	CH_3CN	6	99.0	0.05	6
BiOCl	CH_3CN	10	99.0	0.1	7
Porous organic polymer (POP) CF-HCP	CH_3CN	6	80.6	6.0	8
Rh/carbon nanotube	$CHCl_3/H_2O$	13	95	7.3	9
Cu-based polyoxometalate	CH_3CN	16	95	12.5	10
PCN-222	CH_3CN	1	100	25.7	5
1	DMF	2	99	22.9	This work

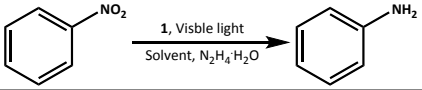
Table S8. Photoreduction of nitrobenzene under various conditions.[a]



Entry	Photocatalyst	$N_2H_4·H_2O$	Light	Conv. [%][b]
1	-	+	+	-
2	+	+	-	-
3	+	-	+	-
4	+	+	+	99
5[c]	+	+	+	74
6[d]	+	+	+	44

[a]Reaction conditions: 0.1 mmol nitrobenzene, 5 mg **1**, 4mmol $N_2H_4·H_2O$, 1 mL EtOH, 4 hour under visible light. [b]Determined by GC using *n*-decane as the internal standard. [c]3mmol $N_2H_4·H_2O$. [d]5 mmol $N_2H_4·H_2O$.

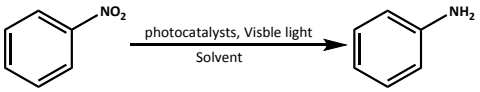
Table S9. Solvent influence on photoreduction of nitrobenzene over **1.**[a]



Solvent	T [h]	Yield. [%][b]
EtOH	4	99
MeCN	6	99
AcOEt	6	70
DMSO	8	99
DMF	8	99
$CHCl_2$	12	99
$CHCl_3$	12	53

[a]Reaction conditions: 0.1 mmol nitrobenzene, 5 mg **1**, 1 mL solvent, 4 mmol hydrazine. [b]Reactions were analysed by GC using *n*-decane as the internal standard.

Table S10. Performances of visible-light-induced photoreduction of nitrobenzene using various photocatalysts at room temperature.



Catalyst	Solvent	T [h]	Yield. [%]	TOF [h^{-1}]	Refs
CdS	water	4	99	1.4	11
Eosin Y	EtOH/H_2O	24	99	4.2	12
Ag/GO/LDH	Benzyl alcohol	4	47	7.0	13
Au/GO/LDH	Benzyl alcohol	4	68	4.4	13
AuAg/GO/LDH	Benzyl alcohol	3	91.6	10.9	13
1	EtOH	4	99	5.8	This work

References

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