

Supplementary material

Visible-light-driven photocatalytic selective oxidation of amines and sulfides over a vanadium metal-organic framework

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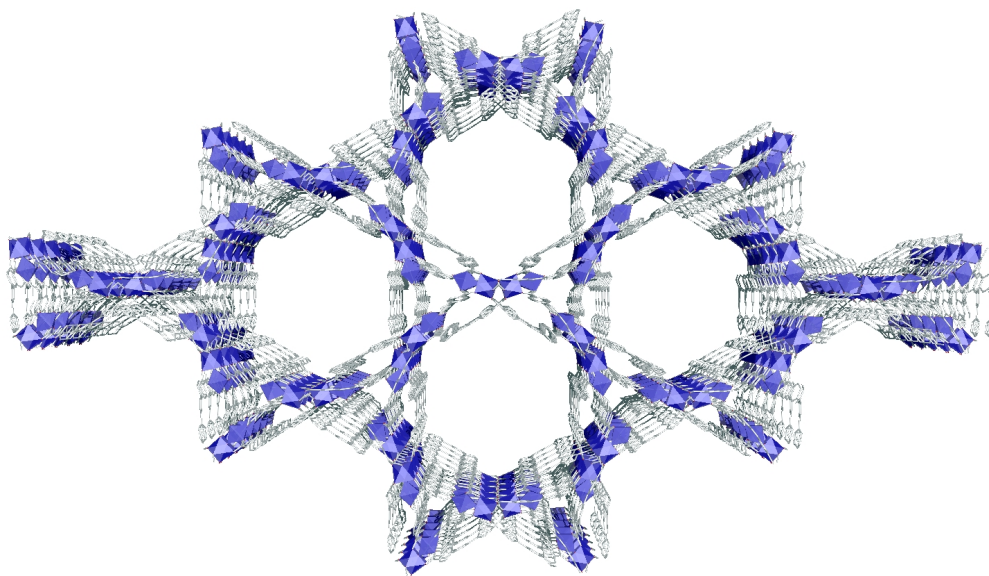


Fig. S1. Structure of BIT-66.

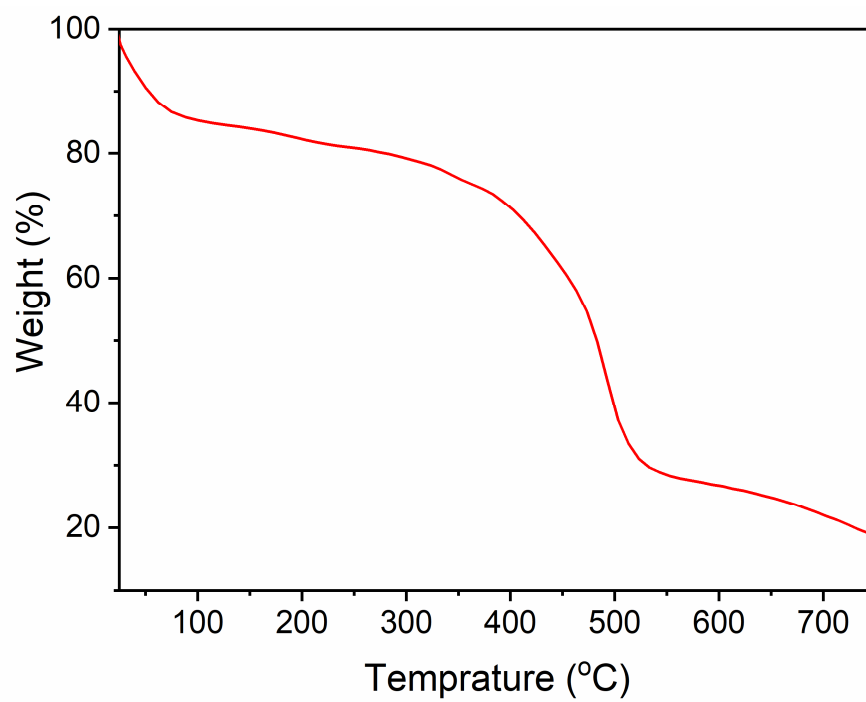


Fig. S2. TGA curve of the as-synthesized BIT-66.

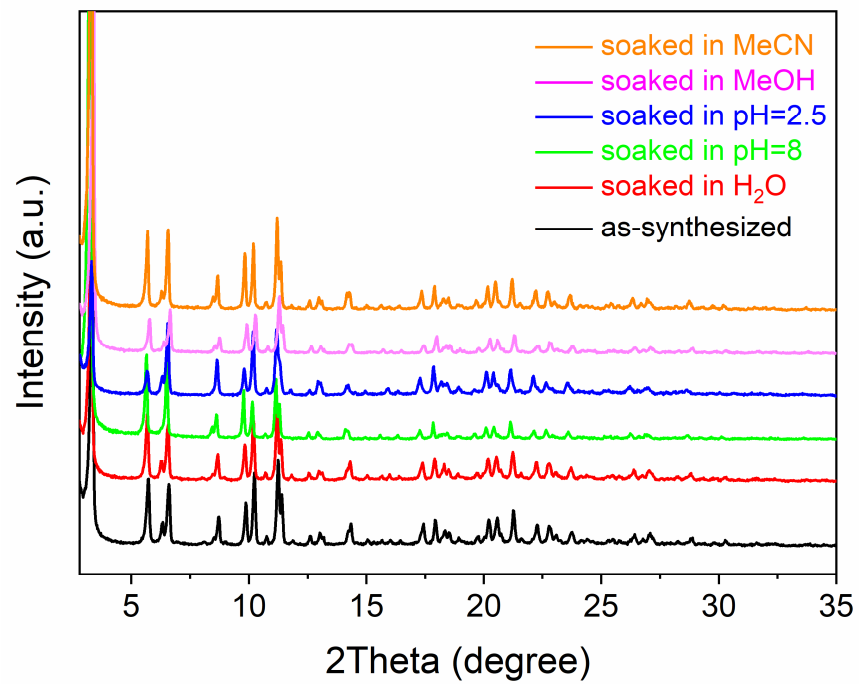


Fig. S3. PXRD patterns of the prepared BIT-66 after immersing in different solutions for 12 h.

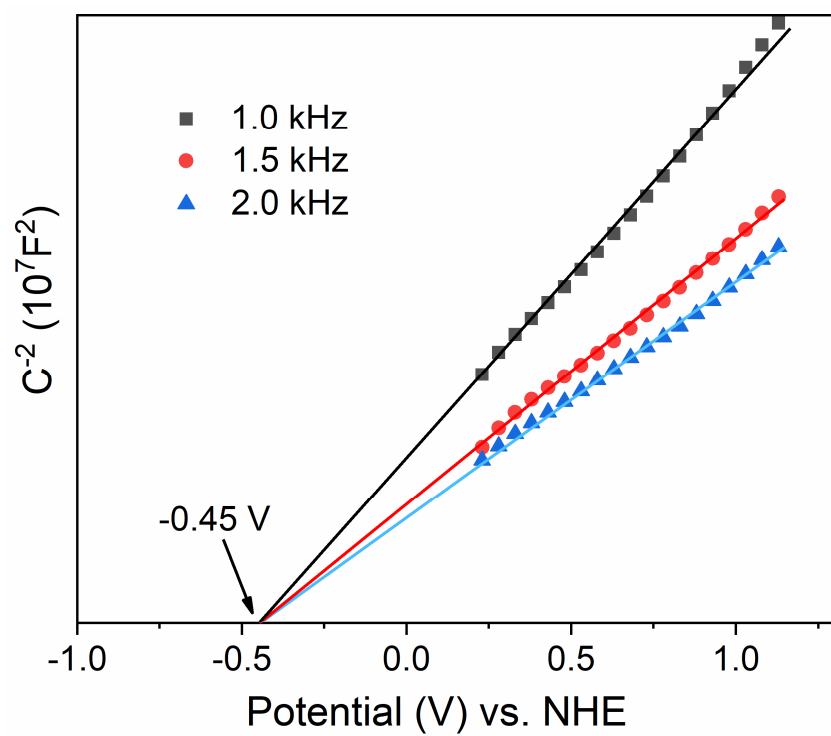


Fig. S4. Mott-Schottky plots of the as-synthesized BIT-66.

Table S1. Photocatalytic oxidative coupling of benzylamine under various reaction conditions^a

Entry	Solvent	Oxidant	Light	Conv. (%)	Sel. (%)
1	MeCN	O ₂	On	85	99
2	DMF	O ₂	On	70	99
3	H ₂ O	O ₂	On	16	99
4	Toluene	O ₂	On	20	99
5	MeCN	Ar	On	7.6	- ^b
6	MeCN	O ₂	Off	-	-
7 ^c	MeCN	O ₂	On	-	-
8 ^d	MeCN	H ₂ O ₂	Off	-	-
9 ^d	MeCN	H ₂ O ₂	On	7.9	-

^a Reaction conditions: 5 mg of BIT-66, 0.5 mmol of benzylamine, 5 mL of solvent, 12 h of visible light irradiation ($800 \text{ nm} \geq \lambda \geq 420 \text{ nm}$).

^b No detected.

^c Without BIT-66.

^d 15 mM H₂O₂ was used under Ar atmosphere.

Table S2. Photocatalytic oxidative coupling of benzylamine over different pure MOFs

photocatalysts under visible light irradiation

Entry	Photocatalyst	Oxidant	TOF (h ⁻¹) ^a	Ref.
1	NH ₂ -MIL-125(Ti)	O ₂	2.0	[1]
2	Cd(dcbpy)	Air	2.4	[2]
3	ZJU-56	O ₂	3.5	[3]
4	Zn-bpydc	Air	4.2	[4]
5	BIT-66	O ₂	7.7	This work
6	FJI-Y10	O ₂	8.3	[5]
7	In-ADBEB	O ₂	11.0	[6]
8	PCN-222	Air	24.6	[7]
9	Zn ₃ (OH) ₂ (ADBEB) ₂	O ₂	45.8	[8]

^a The turnover frequency (TOF) values were calculated as the moles of the converted benzylamine divided by the moles of photocatalyst and the reaction time.

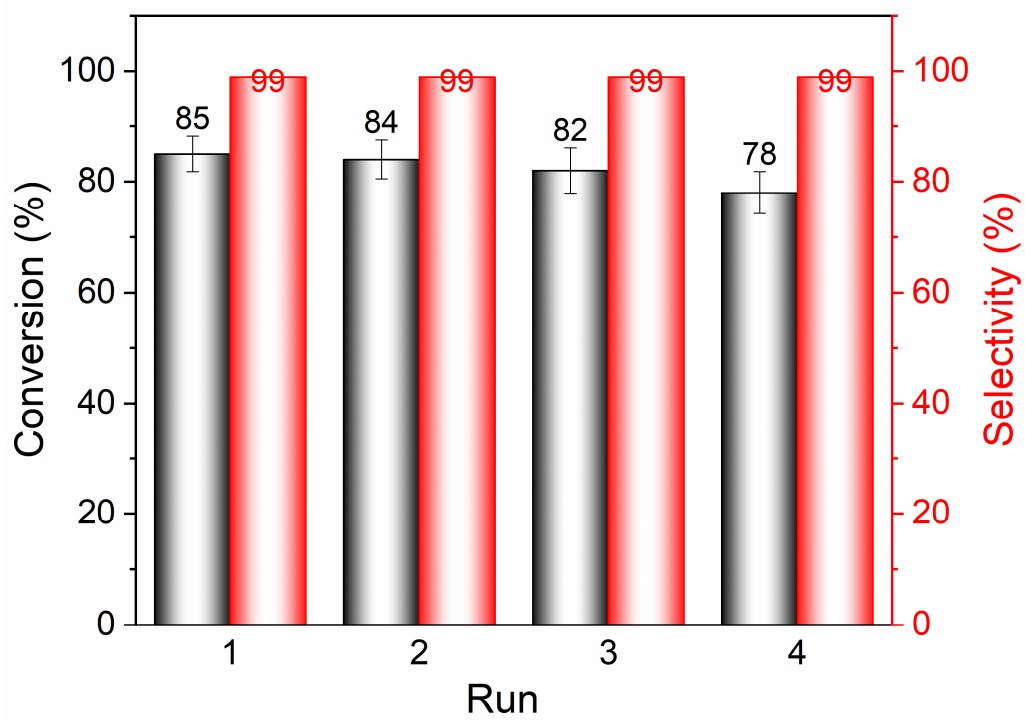


Fig. S5. Reusability of BIT-66 in the photocatalytic oxidative coupling of benzylamine upon visible-light irradiation.

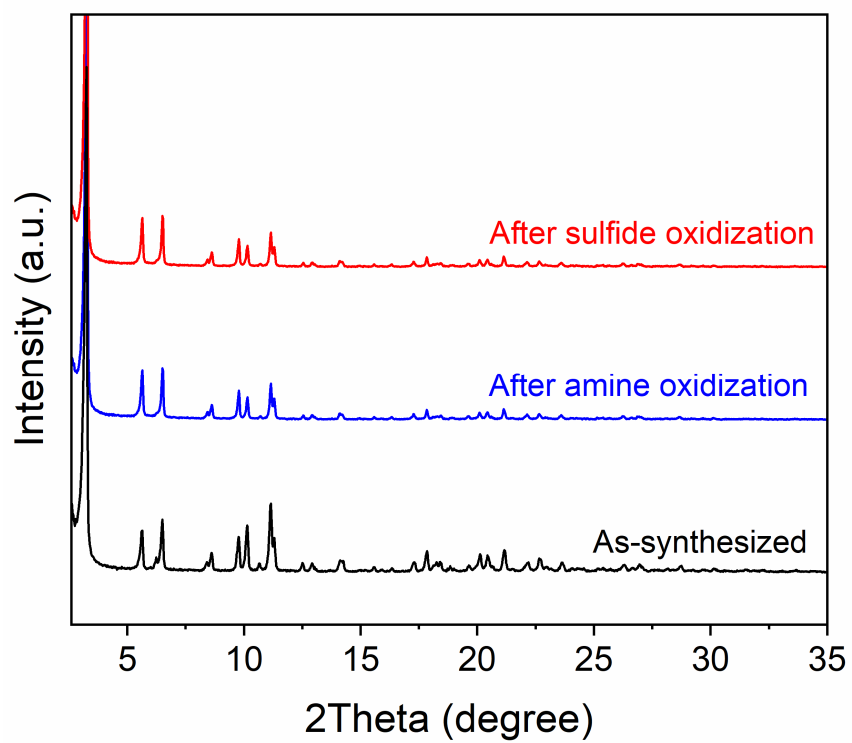


Fig. S6. PXRD patterns of the fresh and the used BIT-66 after the 4th-run photocatalytic reaction.

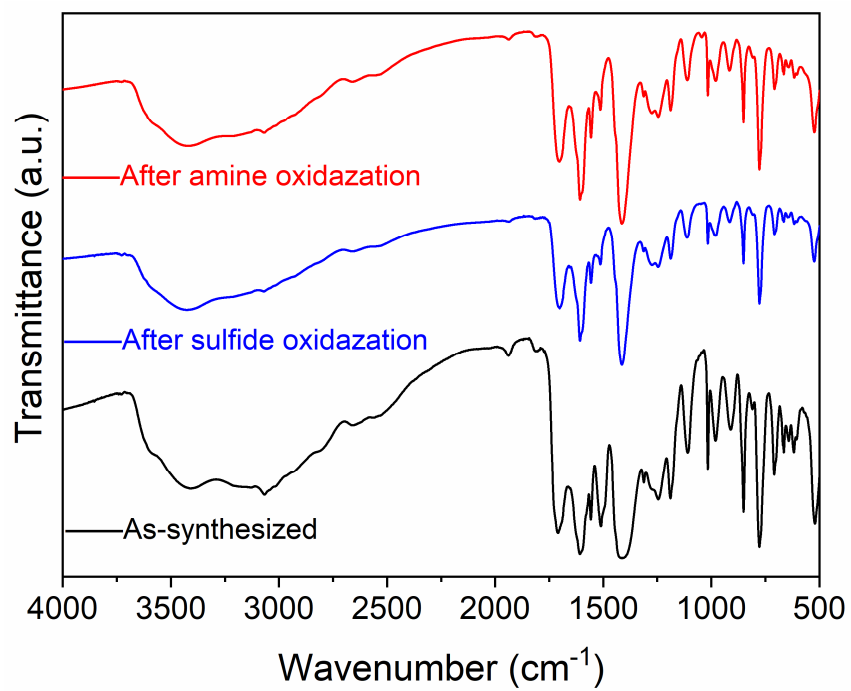


Fig. S7. FT-IR spectra of the fresh and the used BIT-66 after the 4th-run photocatalytic reaction.

Table S3. Photocatalytic oxidation of thioanisole under various reaction conditions^a

Entry	Solvent	Oxidant	Conv. (%)	Sel. (%)
1	MeCN	O ₂	-	-
2	MeCN	H ₂ O ₂	90	53
3	MeCN	TBHP	97	98
4	MeOH	TBHP	80	98
5	H ₂ O	TBHP	32	98
6 ^b	MeCN	TBHP	-	-
7 ^c	MeCN	TBHP	9	98

^a Reaction conditions: 5 mg of BIT-66, 1.5 mmol of thioanisole, 1.5 mmol of oxidant, 5 mL of solvent, 3 h of visible light irradiation ($800 \text{ nm} \geq \lambda \geq 420 \text{ nm}$).

^b Without BIT-66.

^c In dark.

Table S4. Photocatalytic oxygenation of thioanisole over different pure MOFs photocatalysts under visible light irradiation^a

Entry	Photocatalyst	Oxidant	TOF (h ⁻¹) ^a	Ref.
1	PCN-222(Zr)	Air	1.5	[9]
2	DUT-67(Zr)	O ₂	1.9	[10]
3	CoMo-TPT	O ₂	2.6	[11]
4	Zr ₆ -IrbpyOMe	O ₂	3.4	[12]
5	Zr ₁₂ -NBC	Air	5.0	[13]
6	Zr-TCA	Air	5.0	[14]
7	Bi-PMOF	O ₂	6.3	[15]
8	In-ADBEB	H ₂ O ₂	14.7	[6]
9	[Ru(bpy) ₃]Cl ₂ -UiO-67	Air	16.6	[16]
10	UNLPF-10	Air	103.9	[17]
11	BIT-66	TBHP	105.7	This work

^a The turnover frequency (TOF) values were calculated as the moles of the converted thioanisole divided by the moles of photocatalyst and the reaction time.

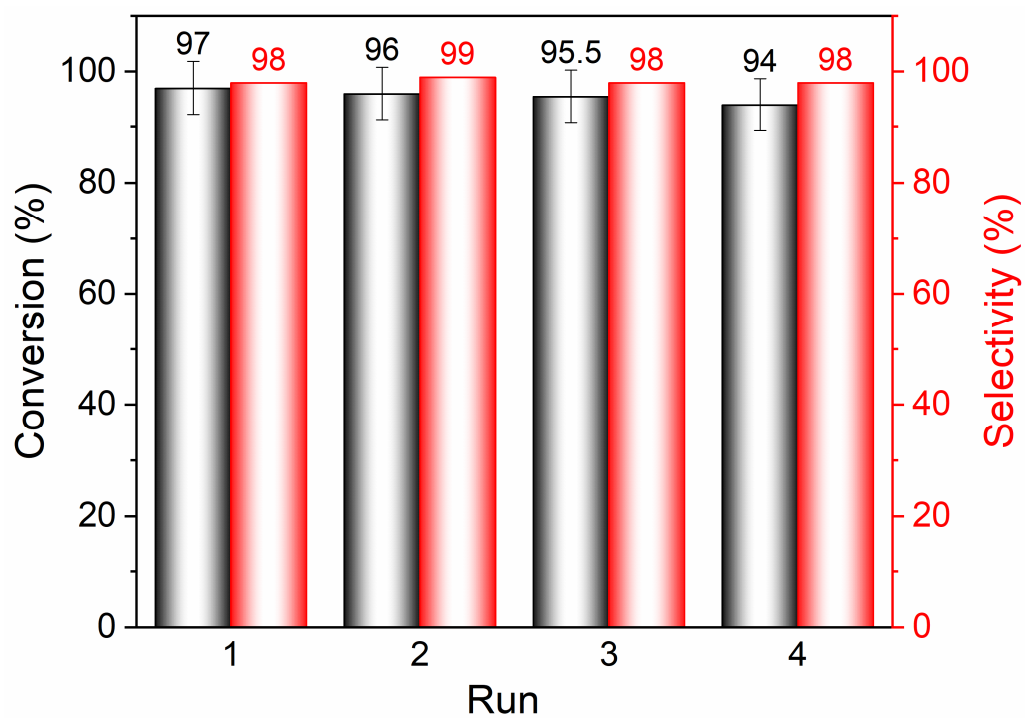


Fig. S8. Reusability of BIT-66 in the photocatalytic oxygenation of thioanisole upon visible-light irradiation.

Table S5. Quenching experiments for the photocatalytic oxidation of benzylamine and thioanisole^a

Entry	Substrate	Oxidant	Scavenger	Inhibited species	Conv. (%)
1	Benzylamine	O ₂	-	-	85
2		O ₂	<i>p</i> -BQ	•O ₂ ⁻	12
3		O ₂	AgNO ₃	e ⁻	26
4		O ₂	EDTA	h ⁺	58
5		O ₂	IPA	•OH	83
6		O ₂	2-Methylfuran	¹ O ₂	83
7	Thioanisole	TBHP	-	-	97
8		TBHP	IPA	•OH	44
9		TBHP	AgNO ₃	e ⁻	33
10		TBHP	EDTA	h ⁺	40
11		TBHP	<i>p</i> -BQ	^t BuOO•	59
12		TBHP	2-Methylfuran	¹ O ₂	95

^a The reaction conditions were similar to those for the photocatalytic oxidation of benzylamine and thioanisole except that 1 mmol of the scavenger agent was added into the reaction system before visible light irradiation.

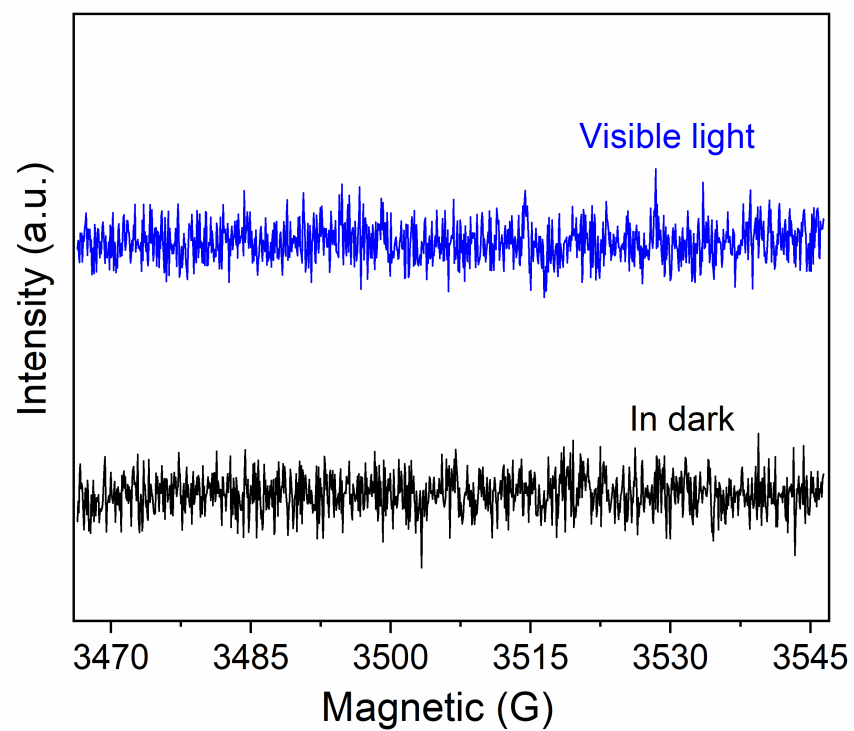


Fig. S9. EPR detection of the $\cdot\text{OH}$ species trapped by DMPO in the photocatalytic oxidative coupling of benzylamine over BIT-66.

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