## Supporting Information

Enhanced photocatalytic activity of Fe@UiO-66 for aerobic oxidation of

N-aryl tetrahydroisoquinolines

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## **Chemicals and materials**

Zirconium tetrachloride (ZrCl<sub>4</sub>, 99%) was purchased from Sigma-Aldrich. 1,4dicarboxybenzene (>98%), hydrochloric acid (37 wt%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Ferrocene (99.99%) was purchased from Jiangsu MNT Micro and Nanotech Co., Ltd. The other chemicals and solvents were purchased from Bidepharm and Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

## Characterization

UiO-66 and Fe@UiO-66 samples were degassed at 423 K for 12 h before measuring the N<sub>2</sub> sorption isotherms on a Micromeritics 3Flex 3.01 instrument at 77 K. The powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation operated at 40 kV, 40 mA. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured using a Bruker Avance III device with a frequency of 400 MHz. Thermogravimetric analysis (TGA) was conducted on the TA Q500 instrument under a 100 mL/min flow of  $N_2,$  ramping from 50 °C to 700 °C at a rate of 10 °C/min. Scanning electron microscopy (SEM) images were recorded on the Hitachi SU-8010 instrument. Transmission electron microscopy (TEM) images were recorded on the Hitachi HT-7700 instrument. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Thermo Scientific K-Alpha analyzer with an Al Kα (1486.6 eV) X-ray source, and the binding energy was calibrated by the C 1s peak (284.8 eV). Electron paramagnetic resonance (EPR) spectra were recorded by Bruker (A300) EPR spectroscopy. UV-Vis diffuse reflectance spectra were recorded on a SHIMADZU UV-2600i spectrometer, using BaSO<sub>4</sub> as the reference. The inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by a Varian-730ES atomic absorption spectrometer. The samples for ICP-OES measurement were digested in HNO<sub>3</sub> aqueous solution at 160 °C for 4 h. The state photoluminescence (PL) spectrum was recorded at room temperature by Edinburgh FLS1000.

Photoelectrochemical measurements were obtained on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China). The working electrodes were prepared by dropping the sample suspension (10  $\mu$ L), which was

obtained from the mixture of as-synthesized samples (5 mg), 30  $\mu$ L Nafion, and 1 mL ethanol under sonication for 30 min, onto the surface of glassy carbon electrode. After drying at room temperature, electrochemical measurements were performed in a standard three-electrode system with the photocatalyst-coated glassy carbon electrode as the working electrode, Pt plate as the counter electrode, and Ag/AgCl as a reference electrode. A 300 W Xenon lamp (HDL-II, Bobei Light Co. Ltd) was used as the light source. A 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. The photoresponsive signals of the samples were measured at 0.3 V. And the electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 10<sup>-1</sup> to 10<sup>5</sup> Hz with a bias potential of 0.2 V.



Figure S1. SEM images of (a) Fe@UiO-66-2c, (b) Fe@UiO-66-3c.



Figure S2. TEM and EDS mapping images of (a) Fe@UiO-66-2c, (b) Fe@UiO-66-3c.



Figure S3. Cross-sectional TEM images of Fe@UiO-66-1c. (a) TEM image and (b, c) EDS line scan results along with the white line. (d-f) EDS elemental mapping of the selected region.



Figure S4. TEM images of (a) Fe@UiO-66-1c, (b) Fe@UiO-66-2c, (c) Fe@UiO-66-3c and HRTEM images of (d) Fe@UiO-66-1c, (e) Fe@UiO-66-2c, (f) Fe@UiO-66-3c.



Figure S5. TGA curves of the Fe@UiO-66 samples under  $N_2$  atmosphere.



Figure S6. DFT pore size distributions for UiO-66 samples.



Figure S7. Zr 3d XPS of UiO-66 and Fe@UiO-66-1c.



Figure S8. Mott–Schottky plots of UiO-66.



Figure S9. (a) EIS Nyquist plots, (b) PL spectra for UiO-66 and Fe@UiO-66-1c.



Figure S10. (a) Recycling test of Fe@UiO-66-1c catalyzed aerobic oxidation of *N*-aryl tetrahydroisoquinoline. (b) PXRD patterns of Fe@UiO-66-1c before and after six runs.



Figure S11. SEM image of Fe@UiO-66-1c after six runs.

Table	<b>S</b> 1	Comparison	of	catalyst	performance	in	the	photo-oxidation	of	N-aryl
tetrahy	ydroi	isoquinolines								

Reaction	Catalyzat	Light gauges	Reaction	Yield and	References	
system	Catalyst	Light source	time (h)	substrate		
	rose	blue LEDs	16 49	51-95%,	ACS Catal., 2018, 8,	
	bengal	(12 W)	10-48	19 examples	6659-6664.	
				50 96%	Adv. Synth. Catal.,	
	eosin Y	green LEDs	16-36	30-3070,	2019, <b>361,</b> 1124-	
				28 examples	1129.	
homogeneous	rose	green LEDs	18	23-95%,	Chem. Eur. J., 2019,	
	bengal	(λ=560 nm)	10	15 examples	<b>25</b> , 4062-4066.	
	4 CaIDN	blue LEDs	10	61-84%,	Chem. Asian J., 2022,	
	4-0211 N	(6 W)	10	7 examples	17, e202200878.	
	ZnTPP	blue LEDs	12	54-84%,	Synlett, 2021, <b>32</b> ,	
		(5 W)	12	23 examples	679-684.	
	To Th 6	blue LEDs	12	72-91%,	Catal. Sci. Technol.,	
	1a-111-0	(18 W)	12	12 examples	2022, <b>12</b> , 1202-1210.	
	D COE 1	blue LEDs	12 15	32-93%,	Chem. Eur. J., 2021,	
hotomogonooug	2D-COF-1	(40W, 456 nm)	12-13	21 examples	<b>27</b> , 7738-7744.	
neterogeneous	a C N	hlua I EDa	o 71	41-73%,	Green Chem., 2019,	
	g-C <sub>3</sub> N <sub>4</sub>	olue LEDS	0-24	12 examples	<b>21</b> , 6116-6122.	
	Fe@UiO-	white LEDs	o 71	43-94%,	This work	
	66-1c	(10 W)	8-24	9 examples		

Characterization data of products



Pale yellow solid, 87% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.26 (dd, J = 23.8, 8.1 Hz, 3H), 6.94 (d, J = 8.8 Hz, 2H), 3.94 (t, J = 6.5 Hz, 2H), 3.82 (s, 3H), 3.13 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.4, 157.8, 138.3, 136.1, 131.9, 129.8, 128.7, 127.2, 127.0, 126.7, 114.3, 55.5, 49.7, 28.7.



White solid, 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, J = 7.7 Hz, 1H), 7.46 (td, J = 7.4, 1.2 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 8.2 Hz, 1H), 7.24 (t, J = 6.6 Hz, 1H), 7.02 – 6.92 (m, 2H), 6.86 – 6.77 (m, 1H), 3.97 (t, J = 6.5 Hz, 2H), 3.81 (s, 3H), 3.13 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.2, 160.0, 144.3, 138.3, 132.1, 129.7, 129.6, 128.7, 127.2, 127.0, 117.5, 112.2, 111.4, 55.4, 49.5, 28.6.



Pale yellow solid, 77% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 – 8.06 (m, 1H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.14 (m, 5H), 3.96 – 3.88 (m, 2H), 3.09 (t, *J* = 6.5 Hz, 2H), 2.32 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.3, 140.5, 138.3, 136.1, 131.9, 129.8, 129.6, 128.7, 127.2, 126.9, 125.2, 49.5, 28.6, 21.1.



White solid, 80% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.44 (m, 3H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.21 (m, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.16 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.2, 146.0, 138.2, 132.5, 129.2, 128.8, 127.8 (d, *J*<sub>CF</sub> = 32.7 Hz), 127.4, 127.1, 125.9 (q, *J*<sub>CF</sub> = 3.8 Hz), 125.3, 124.1 (q, *J*<sub>CF</sub> = 271.9 Hz), 49.1, 28.5.



White solid, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, J = 7.4 Hz, 1H), 7.49 (td, J = 7.5, 1.2 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.26 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 8.6 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 3.16 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.4, 160.7 (d,  $J_{CF}$  = 245.7 Hz), 139.0 (d,  $J_{CF}$  = 3.1 Hz), 138.2, 132.2, 129.5, 128.7, 127.3, 127.1, 127.0 (d,  $J_{CF}$  = 3.8 Hz), 115.7 (d,  $J_{CF}$  = 22.7 Hz), 49.6, 28.6.



White solid, 82% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 7.7,1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 – 7.30 (m, 5H), 7.25 (d, *J* = 8.4 Hz,1H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.2, 141.5, 138.2, 132.3, 131.6, 129.4, 129.0, 128.8, 127.3, 127.0, 126.6, 49.3, 28.6.



White solid, 87% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.32 (dd, J = 8.9, 4.9 Hz, 2H), 7.08 (t, J = 8.6 Hz, 2H), 6.69 (s, 1H), 3.95 – 3.92 (m, 8H), 3.06 (t, J = 6.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.4, 160.6 (d,  $J_{CF} = 246.4$  Hz), 152.2, 148.1, 139.2 (d,  $J_{CF} = 2.9$  Hz), 132.1, 127.1 (d,  $J_{CF} = 8.4$  Hz), 121.9, 115.7 (d,  $J_{CF} = 22.6$  Hz), 110.8, 109.2, 56.1, 49.8, 28.2.



White solid, 71% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.69 (s, 1H), 3.94 – 3.91 (m, 8H), 3.82 (s, 3H), 3.06 (t, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.4, 157.7, 152.0, 148.0, 136.3, 132.0, 126.7, 122.2, 114.2, 110.8, 109.2, 56.1, 55.5, 49.9, 28.3.



Light yellow liquid, 43% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.20 (m, 1H), 7.16 (d, J = 6.9 Hz, 1H), 7.01 – 6.98 (m, 2H), 3.93 (t, J = 7.6 Hz, 2H), 2.88 (t, J = 7.6 Hz, 2H), 2.65 – 2.61 (m, 2H), 1.62 (p, J = 7.6 Hz, 2H), 1.39 (dt, J = 14.8, 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.2, 139.6, 128.0, 127.4, 126.6, 122.6, 114.8, 41.9, 31.9, 29.3, 25.6, 20.2, 13.9.

## **Copies of NMR Spectra.**

















