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## **Electronic Supplementary Information**

## Incorporation of Ru Complex into Amine-Functionalized Metal-Organic Framework for Enhanced Activity in Photocatalytic Aerobic Benzylalcohol Oxidation

Yusuke Isaka,<sup>†</sup> Yoshifumi Kondo,<sup>†</sup> Yasutaka Kuwahara,<sup>†,‡</sup> Kohsuke Mori<sup>†,‡,§</sup> and Hiromi Yamashita<sup>\*,†,‡</sup>

<sup>†</sup> Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

<sup>‡</sup> Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan

§ JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

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## **Experimental section**

## **Repetitive photocatalytic reaction**

Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub> (20.0 mg), benzylalcohol (4.0 mL), and acetonitrile (16.0 mL) were added to a Shrenk tube, which was sealed with a rubber septum. The resulting mixture was sonicated and bubbled with oxygen for 15 min in the dark. Subsequently, the sample was irradiated from the side with an Xe lamp (500 W; SAN-EI ELEC- TRIC XEF-501S) through a glass filter ( $\lambda > 450$  nm) at ambient pressure and temperature. An aliquot of the reaction solution was collected and analyzed. The catalyst was recovered from the reaction solution centrifugally after 4 h of each run, washed with fresh acetonitrile and employed for the next run.



Figure S1. N<sub>2</sub> adsorption isotherm of Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub> at 77 K.



**Figure S2.** Gas chromatography chart obtained after 8 h of visible-light irradiation ( $\lambda > 450$  nm) to the acetonitrile solution (5.0 mL) of benzylalcohol (1.0 mL) containing 5.0 mg of Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub>.

The peaks at 4.535 min, 8.666 min and 10.217 min correspond to acetonitrile, benzaldehyde and benzylalcohol, respectively.



**Figure S3.** UV-Vis spectra of supernatant collected after 5.0 mg of Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub> was dispersed in O<sub>2</sub>-saturated acetonitrile (5.0 mL) solution of benzylalcohol (1.0 mL) and irradiated with visible light ( $\lambda > 450$  nm) for 8 h.

Absence of absorption peak around 450 nm due to  $[Ru(bpy)_3]^{2+}$  indicates that leaching did not occur during the photocatalysis. The absorption observed at  $\lambda > 280$  nm is due to benzylalcohol and the small peak around  $\lambda = 320$  nm is attributed to benzaldehyde.



**Figure S4.** Time courses of repetitive benzaldehyde production (1st run: blue, 2nd run: orange, 3rd run: grey) under visible-light irradiation ( $\lambda > 450$  nm) of an acetonitrile suspension (20 mL) containing Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub> (20 mg) and benzylalcohol (4.0 mL). The solid in the reaction suspension was centrifugally collected every 4 h of photoirradiation and employed in the next cycle of reaction after addition of fresh acetonitrile solution (20 mL) of benzylalcohol (4.0 mL).



**Figure S5.** EPR spectra of a suspension (5.0 mL) containing benzylalcohol (1.0 mL), DMPO (10 mM) and 5.0 mg of Ru(bpy)<sub>3</sub>@MIL-125-NH<sub>2</sub> dispersed in acetonitrile after 60 minutes of visible light ( $\lambda >$  450 nm) irradiation in N<sub>2</sub> atmosphere (top) and after 4 minutes of visible light ( $\lambda >$  450 nm) irradiation in air (bottom).



Figure S6. XRD spectrum of Ru(bpy)<sub>3</sub>@MIL-125.