Electronic Supplementary Information

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

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**Experimental section**

**Repetitive photocatalytic reaction**

Ru(bpy)$_3$@MIL-125-NH$_2$ (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. N₂ adsorption isotherm of Ru(bpy)₃@MIL-125-NH₂ 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)$_3$@MIL-125-NH$_2$.

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)$_3$@MIL-125-NH$_2$ was dispersed in O$_2$-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)$_3$@MIL-125-NH$_2$ (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)$_3$@MIL-125-NH$_2$ dispersed in acetonitrile after 60 minutes of visible light ($\lambda > 450$ nm) irradiation in N$_2$ atmosphere (top) and after 4 minutes of visible light ($\lambda > 450$ nm) irradiation in air (bottom).
Figure S6. XRD spectrum of Ru(bpy)$_3$@MIL-125.