Photocatalytic metal-organic frameworks for the aerobic oxidation of arylboronic acids

Xiao Yu and Seth M. Cohen*

Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States

Supporting Information

* To whom correspondence should be addressed. E-mail: scohen@ucsd.edu. Telephone: (858) 822-5596.
**General Methods**

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (\(^1\)H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. A Rayonet Photochemical reactor (Model RPR-200) was used for photocatalysis reactions equipped with near-UV lamps (\(\lambda = 365 \text{ nm}\)). A compact fluorescent bulb (23 W, 1600 lumen) was used as visible-light source. Centrifugation was performed using a Beckman Coulter Allegra X-22R Centrifuge, with a fixed-angle rotor at 6800 rpm for 10 min.

**Experimental Procedures**

*Synthesis of UiO-67-bpy\(_{0.25}\).* ZrCl\(_4\) (120 mg, 0.514 mmol), benzoic acid (1.88g, 15.4 mmol), H\(_2\)bpdc (biphenyldicarboxylic acid, 94 mg, 0.39 mmol), and H\(_2\)bpydc (2,2'-bipyridine-5,5'-dicarboxylic acid, 31 mg, 0.13 mmol) were placed in a vial with 20 mL of DMF. The solids were dispersed via sonication for ~10 min, followed by incubation at 120 °C for 24 h. After cooling, solids were collected by centrifugation and the solvent was decanted. The solids were washed with DMF (2×20 mL), followed by soaking in ethanol (EtOH) for 3 d, and the solution was exchanged with fresh EtOH (10
mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

*Using PSM to prepare UiO-67-[Ru(bpy)]_{3.0.1}.*  
UiO-67-bpy_{0.25} (35.5 mg, 0.1 mmol) and cis-Ru(bpy)$_2$Cl$_2$ (*cis*-bis(2,2'-bipyridine)dichlororuthenium(II) hydrate) (14.6 mg, 0.03 mmol) were placed in a scintillation vial with 1 mL EtOH and 1 mL H$_2$O. The solids were dispersed via sonication for ~10 min, followed by incubation at 80 °C for 2 h. After cooling, solids were collected by centrifugation and the solvent was decanted. The solids were washed once with H$_2$O (20 mL) and twice with EtOH (20 mL), followed by soaking in EtOH for 3 d, with the solution exchanged with fresh EtOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

*Aerobic oxidation reaction catalyzed by UiO-67-[Ru(bpy)]_{3.0.1}.*  
Arylboronic acid (0.5 mmol), *N*,*N*-diisopropylethylamine (0.6 mmol), and UiO-67-[Ru(bpy)]$_{3.0.1}$ (100 mg, 5 mol%) were placed in a 20 mL round-bottom flask with 5 mL MeOH. After sonication for 10 min, the flask was opened to air and put into a photoreactor ($\lambda = 365$ nm) equipped with a cooling fan for 24 h. For visible-light reactions, a 23W compact fluorescent bulb (1600 lumen) was put under the round-bottom flask at a distance of 5 cm. A condenser was connected to the round-bottom flask to prevent solvent evaporation. After the reaction was complete, the supernatant was separated by centrifugation and evaporated before being analyzed by $^1$HNMR (in CD$_3$OD). Some leaching of biphenyl dicarboxylic acid ligand is observed in analysis, and control experiments were performed by soaking
UiO-67-[Ru(bpy)$_3$)$_{0.1}$ in reactants solution without light irradiation (see Fig S12). To test recyclability, the supernatant was decanted from the catalyst after 48 h reaction and the catalyst was washed with MeOH (3×10 mL). The washed MOFs were directly used for the next round oxidation catalysis for the same substrate.

*Powder X-ray Diffraction (PXRD) Analysis.* ~20-30 mg of UiO-67-bpy material was dried under vacuum prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα ($\lambda$= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of ~5 to 45° (sample dependent). The experimental background was corrected using the Jade 5.0 software package.

*Digestion and Analysis by $^1$H NMR.* ~10 mg of UiO-67-bpy material was dried under vacuum and digested with sonication in 600 µL DMSO-$d_6$ and 10 µL of 40% HF. Approximately 10 mg UiO-67-Ru(bpy)$_3$ was suspended in a 0.1 M solution (1 mL) of D$_3$PO$_4$ in D$_2$O/DMSO-$d_6$ (prepared by mixing 11.9 mg of a solution of D$_3$PO$_4$ (85% in D$_2$O) with 1 mL DMSO-$d_6$) and stirred at room temperature for 5 h. The solution was filtered through cotton and placed in an NMR tube.

*BET Surface Area Analysis.* ~50 mg of UiO-67-bpy material was evacuated on a vacuum line overnight at room temperature. The sample was then transferred to a pre-weighed sample tube and degassed at 105 °C on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mm Hg. The sample tube was re-weighed to obtain a consistent mass for the degassed exchanged
MOF. BET surface area (m$^2$/g) measurements were collected at 77 K by N$_2$ on a Micromeritics ASAP 2020 Adsorption Analyzer using the volumetric technique, and the surface areas reported for each material is the average of three independent samples.

*Thermalgravimetric Analysis.* ~10-15 mg of UiO-67-bpy material was used for TGA measurements, after BET analysis (activated). Samples were analyzed under a stream of N$_2$ using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.
Figure S1. PXRD of UiO-67-bpy0.5, UiO-67-bpy1.0, and their metalated derivatives (PSM for 1 h).

Figure S2. TGA of UiO-67-bpy0.25 (blue) and UiO-bpy-[Ru(bpy)_3]_0.1 (red).
Figure S3. N$_2$ isotherms of UiO-67-bpy$_{0.25}$ and UiO-67-[Ru(bpy)$_3$]$_{0.1}$
**Figure S4.** Top: $^1$HNMR of 5 cycles of aerobic oxidation of phenylboronic acid using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst under near-UV irradiation (peaks for substrate and product are labeled): Run 1 (dark red, yield 81%); Run 2 (orange, yield 72%); Run 3 (green, yield 74%); Run 4 (blue, yield 73%); and Run 5 (dark magenta, yield 57%). Bottom: $^1$HNMR of phenyl boronic acid (black), phenol (brown) and 3 cycles of aerobic oxidation of phenylboronic acid using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst under visible-light irradiation: Run 1 (dark red, yield 85%); Run 2 (orange, yield 78%); Run 3 (green, yield 78%). Some dbp$^2$ ligand (✱) is observed in the reaction mixture after photocatalysis (see Fig. S8).
Figure S5. $^1$HNMR of 4-methoxyphenylboronic acid (black), 4-methoxyphenol (brown), aerobic oxidation of 4-methoxyphenylboronic acid using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst under visible-light irradiation (dark green, Yield 72%) and 5 cycles under near-UV irradiation: Run 1 (dark red, Yield 76%), Run 2 (orange, Yield 72%), Run 3 (green, Yield 72%), Run 4 (dark blue, Yield 73%) and Run 5 (dark magenta, Yield 66%).
**Figure S6.** PXRD of 5 cycles of UiO-67-[Ru(bpy)$_3$)$_{0.1}$ catalyst.

**Figure S7.** $^1$HNMR of digested UiO-67-[Ru(bpy)$_3$]$_{0.1}$ before (red) and after (blue) catalysis showing minimal or no loss in Ru(bpy)$_3$ from the MOF.
**Figure S8.** $^1$H NMR of oxidation of phenylboronic acid using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst (before reaction, magenta; after reaction, dark red) and UiO-67-bpy$_{0.25}$ as catalyst (after reaction, dark blue). Both reaction mixtures show some degree of dcbp$^{2-}$ ligand ($\times$) before and after photocatalysis. The dcbp$^{2-}$ ligand may be leaching from within the MOF (incomplete washing, trapped in pores) or from the MOF itself (partial degradation). Peaks denoted with asterisks represent a small amount of unidentified impurities.
Figure S9. $^1$HNMR of 3-methoxyphenylboronic acid (dark red), 3-methoxyphenol (brown), and the reaction mixture after photocatalysis under visible-light irradiation (dark green, yield ~72%) and near-UV light irradiation (dark blue, yield ~79%). Some dcbp$^{2-}$ ligand (×) is observed in the reaction mixture after photocatalysis (see Fig. S8).
Figure S10. $^1$HNMR of 4-(methoxycarbonyl)phenylboronic acid (dark red), methyl 4-hydroxybenzoate (brown), and the reaction mixture after photocatalysis under both visible light (dark green, yield $> 95\%$) and near-UV irradiation (dark blue, yield $> 95\%$).
Figure S11. $^1$HNMR of 4-fluorophenylboronic acid (dark red), 4-fluorophenol (brown), and the reaction mixture after photocatalysis under both visible-light irradiation (dark green, yield ~50%) and near-UV irradiation (dark blue, yield ~55%). Some dcbp$^{2-}$ ligand (★) is observed in the reaction mixture after photocatalysis (see Fig. S8).
**Figure S12.** $^1$HNMR of 1,4-phenylenediboronic acid (dark red), hydroquinone (brown), and the reaction mixture after reaction under visible-light irradiation (dark green, yield 15%) and near-UV irradiation (dark blue, yield 23%). Peaks denoted with asterisks are from benzoquinone, the oxidation product of hydroquinone. dcbp$^2^-$ ligand (✱) is observed in the reaction mixture after photocatalysis (see Fig. S8).
Figure S13. ¹H NMR of phenylboronic acid pinacol ester (dark red), phenol (brown) and the reaction mixture after photocatalysis under both visible-light (dark green, yield 91%) and near-UV irradiation (dark blue, yield > 95%).