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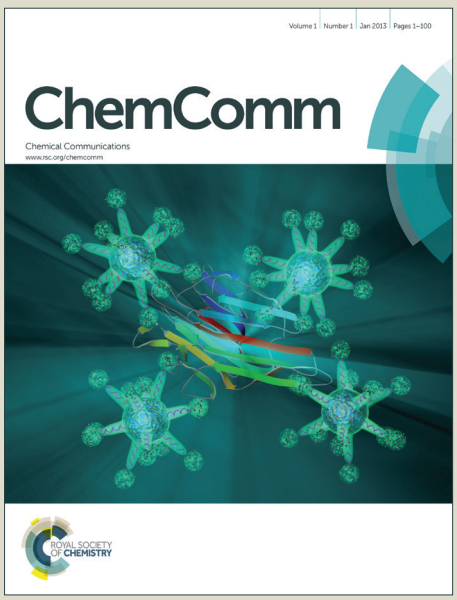

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Photocatalytic metal-organic frameworks for the aerobic oxidation of arylboronic acids

Cite this: DOI: 10.1039/x0xx00000x

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ooth January 2015,
Accepted ooth January 2015

DOI: 10.1039/x0xx00000x

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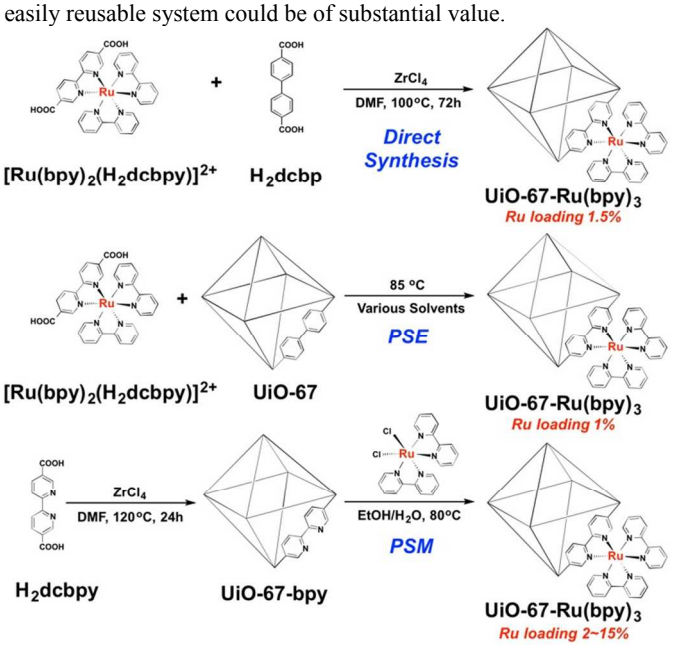
A photocatalytic Ru complex was incorporated into a Zr(IV)-based metal-organic framework (MOF) via postsynthetic methods. The resulting UiO-67-Ru(bpy)$_3$ shows efficient and recyclable catalytic activity for the aerobic oxidation of arylboronic acids under near-UV and visible light irradiation.

Metal-organic frameworks (MOFs) are an emerging class of porous materials that have a wide range of applications, such as gas storage/separation,[1,2] biomedicine,[3] chemical sensors,[4] catalysis,[5] and other technologies.[6] The tunable nature of the organic components in MOFs allows for significant advantages when compared to other porous materials, such as zeolites, which cannot be as readily functionalized. Both pre- and post-synthetic methods have been studied to extend the variety of functionalized MOFs that can be prepared.[7, 8]

Photoactive MOFs have attracted increasing attention for use in a variety of catalytic applications.[9] Mahata et al. first reported the use of a MOF as a photocatalyst to degrade organic pollutants in 2006.[10] The majority of studies on photoactive MOFs have focused on functionalization of MOFs to achieve light harvesting and drive H_2 evolution and CO_2 reduction.[11] Also, Li and co-workers incorporated Ru carbonyl complexes into a MOF for photocatalytic CO_2 reduction under visible-light irradiation.[12] The ability of amine-functionalized MOFs to undergo photoinduced charge separation was demonstrated in several reports, exhibiting photochemical CO_2 reduction activities.[13-17] In other studies, MOFs were shown to catalyze organic transformations under light irradiation.[18] Duan and co-workers incorporated a triphenylamine photoredox group into Zn-based MOFs, which can drive a light-driven α-alkylation reaction.[19]

During the last decade, Ru(bpy)$_3$ and related complexes have been shown to be efficient photocatalysts for organic synthesis.[20] The Yoon and MacMillan groups first employed Ru(bpy)$_3$ to perform [2+2] cycloadditions[21] and α-alkylation of aldehydes,[22] respectively. Stephenson and co-workers disclosed a photoredox reductive dehalogenation of activated alkyl halides mediated by Ru(bpy)$_3$.[23] Ru(bpy)$_3$ and Ir(bpy)$_3$ have also been used in aza-Henry reactions,[24] aerobic amine coupling,[25] hydroxylation of arylboronic acids,[26] sulfide oxidation,[27] and radical chemistry.[28] Considering the high cost of these precious metal based photocatalysts, a heterogeneous, easily reusable system could be of substantial value.



Scheme 1. Synthesis of UiO-67-Ru(bpy)$_3$ using three different synthetic strategies.

To produce such a recyclable catalyst, the Lin group reported doping MOFs with Ru and Ir complexes via direct solvothermal synthesis to produce MOFs that catalyze the aza-Henry reaction, an amine coupling, and oxidation of thioanisole.[29] In addition to this important report, there remain many other reactions of interest and improvements to the catalyst performance, crystallinity, and loading that are yet to be achieved.

MOFs with the ability to catalyze aerobic oxidations have been developed in recent years, which utilize molecular oxygen as a green oxidant.[30, 31] Herein, we incorporate a Ru phtocatalyst into a robust UiO-67 (UiO = University of Oslo) framework via postsynthetic modification (PSM) to get nearly quantitative metal loadings with

retention of crystallinity and porosity. The resulting MOFs exhibit efficient photocatalytic activity for aerobic oxidation of arylboronic acids to the corresponding phenols under light irradiation. Importantly, MOFs serve as a matrix to enhance the stability of the active sites, achieving recyclable catalytic performance over five cycles without significant loss of activity.

The robust UiO-67 framework, consisting of Zr(IV)-based secondary building blocks ($Zr_6O_4(OH)_4$) and biphenyl ligands, was selected as a platform to incorporate $[Ru(bpy)_2(dcbpy)]^{2+}$ (bis(2,2'-bipyridine)(5,5'-dicarboxy-2,2'-bipyridine)ruthenium(II)). Attempts to directly synthesize UiO-67-Ru(bpy)$_3$ gave low loadings of Ru, presumably due to the steric bulk of the complex.[29] We also employed a postsynthetic exchange (PSE) approach[32] to substitute the biphenyl ligand in UiO-67 with $[Ru(bpy)_2(H_2dcbpy)]Cl_2$; however, no enhancement of Ru loading, compared to direct synthesis, was observed under the PSE conditions used (85 °C for 24 h in DMF, MeCN, or EtOH/H_2O). Therefore, we turned to PSM to improve the incorporation of the Ru(II) complex (Scheme 1).

Using a mixed ligand strategy, H_2dcbpy ([2,2'-bipyridine]-5,5'-dicarboxylic acid) and H_2dcbp ([1,1'-biphenyl]-4,4'-dicarboxylic acid) were used to obtain a mixed MOF containing both ligands.[33] Solvothermal synthesis using a molar ratio of 1:3 of H_2dcbpy and H_2dcbp with $ZrCl_4$ and benzoic acid (as modulator) in DMF at 120 °C for 24 h gave a UiO-67 derivative containing ~25% of the dcbpy^{2-} ligand (UiO-67-bpy$_{0.25}$). Postsynthetic modification (PSM, Scheme 1) via a metalation of this MOF with 0.3 equivalents of $Ru(bpy)_2Cl_2$ in EtOH/H_2O at 80 °C for 2 h, followed by centrifugation and washing with fresh EtOH for 3 days, afforded the desired UiO-67-Ru(bpy)$_3$ with ~10% Ru loading (UiO-67-$[Ru(bpy)_3]_{0.1}$). PSM metalation of UiO-67 derivatives containing a higher percentage of dcbpy^{2-} (50~100%) resulted in a loss of framework stability, as evidenced by powder X-ray diffraction (PXRD, Fig. S1).

The formation of Ru complexes and the degree of PSM were clearly characterized by ^{1}H NMR after digesting UiO-67-Ru(bpy)$_3$ in D_3PO_4/DMSO-d_6. This analysis was possible because $Ru(bpy)_2$(dcbpy) remains intact under these MOF digestion conditions. Integration of the proton resonances for $Ru(bpy)_2$(dcbpy) and dcbp^{2-} confirmed the degree of Ru modification, which could be tuned from 2% to 15% by varying the reaction time from 1~24 h (Fig. 1). PXRD confirmed the retention of the UiO-67 topology (Fig. 1) after metalation. The TGA trace of UiO-67-$[Ru(bpy)_3]_{0.1}$ exhibits a decomposition temperature of ~400 °C, which is ~100 °C lower than that of the unmetalated MOF (Fig. S2). In addition, UiO-67-$[Ru(bpy)_3]_{0.1}$ exhibited a BET surface area of 1803±164 m^2/g, which is high, but lower than the BET surface area of the parent MOF UiO-67-bpy$_{0.25}$ (2425±25 m^2/g, Fig. S3).

It is well known that phenols are among the most important intermediates and building blocks in the pharmaceutical and chemical industry.[34] Arylboronic acids can be hydroxylated by strong oxidizing agents such as oxone, hydrogen peroxide, or *meta*-chloroperoxybenzoic acid (MCPBA), which are usually used in stoichiometric amounts and carefully controlled to avoid over-oxidation.[35-38] In pursuit of environmentally friendly methods, Cu(II) and Pd(II) catalysts have been investigated for oxidative hydroxylation of arylboronic acids with molecular oxygen, albeit using a stoichiometric strong base (KOH or NaOH).[39-41] Scaiano et al. reported the photocatalytic hydroxylation of boronic acids with methylene blue as photosensitizer with high efficiency.[42] Xiao and co-workers reported photocatalytic aerobic oxidative hydroxylation mediated by a Ru complex.[26] However, the use of a homogeneous $Ru(bpy)_3^{2+}$ catalyst poses challenges including product separation and high cost. Herein, UiO-67-$[Ru(bpy)_3]_{0.1}$ is shown to act as an efficient and recyclable heterogeneous photocatalyst for aerobic oxidative hydroxylation of arylboronic acids.

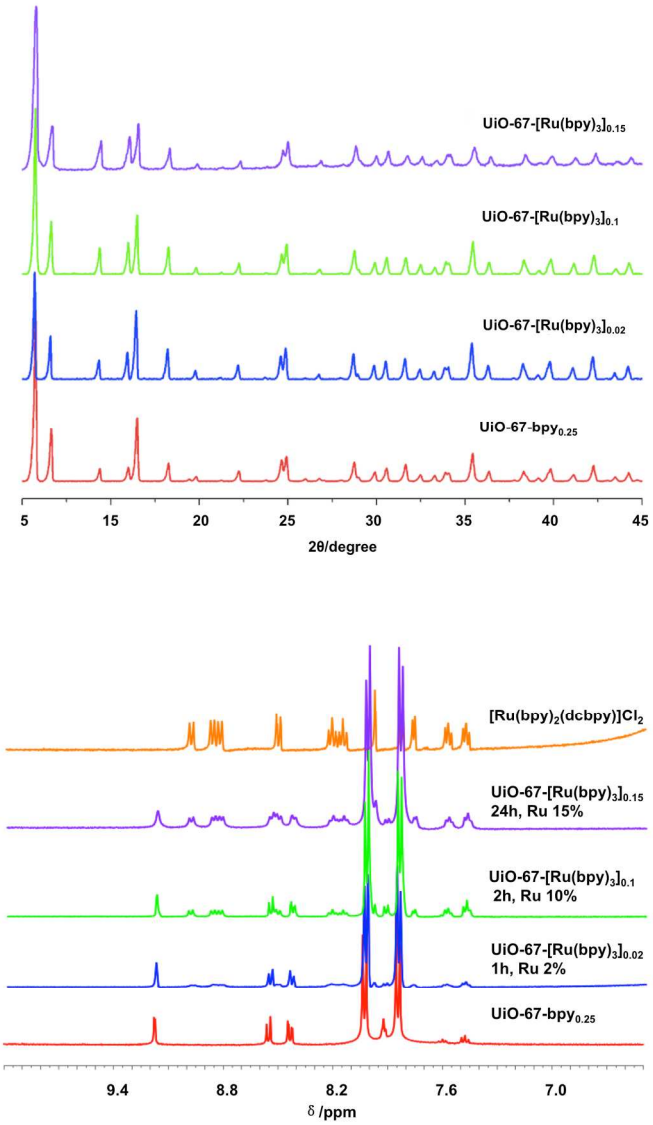


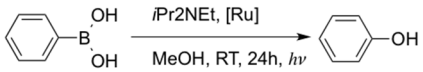
Figure 1 ^{1}H NMR (D_3PO_4/d^6-DMSO digested, bottom) and PXRD (top) of UiO-67-Ru(bpy)$_3$ containing different amount of Ru complex.

As a benchmark reaction, phenylboronic acid was chosen as a substrate. As shown in Table 1, incubating a mixture of phenylboronic acid, *N,N*-diisopropylethylamine (*i*Pr$_2$NEt), and UiO-67-$[Ru(bpy)_3]_{0.1}$ as catalyst in MeOH using a photochemical reactor (λ = 365 nm) led to an ~81% yield of phenol after 24 h. Other solvents, such as DMF, H_2O, and CH_3CN produced lower yields than obtained in MeOH. The overall yield (81%) using UiO-67-$[Ru(bpy)_3]_{0.1}$ is good, but slightly lower than a homogeneous reference system ($Ru(bpy)_3Cl_2$, yield ~95%). The lower yield may be due to incomplete light penetration through the MOF material. Interestingly, pristine UiO-67-bpy$_{0.25}$ gave ~22% conversion under irradiation with UV light after 1 day, indicating a photocatalytic ability similar to ZrO_2.[43] However, a control experiment with no photocatalyst showed no conversion upon UV or visible light irradiation (Table 1, Entry 4). No product was observed when the reaction was carried out in the absence of light even in the presence of photocatalyst (Table 1, Entry 5), confirming the photochemical nature of this oxidation. O_2 was confirmed to be the oxidizing agent,

as a control reaction under an N_2 atmosphere also gave no product (Table 1, Entry 6). Heterogeneity of UiO-67-Ru(bpy)$_3$ was confirmed by filtration of the catalyst after 4 h (4 h yield ~10%), which resulted in no further generation of product after another 44 h of irradiation. This suggests that UiO-67-Ru(bpy)$_3$ is a true heterogeneous catalyst with no catalytically active species released into solution.

To examine recyclability, experiments were performed using the same batch of MOF for the oxidation of 4-methoxyphenylboronic acid for 48 h over five successive catalytic cycles. Between each run, the catalyst was recovered by centrifugation, washed with MeOH, and dried under vacuum at room temperature. The catalyst gave good yields, albeit with slightly lower activity after the fourth run (Fig. S4, S5). The lower yield may be due to some loss in the Ru species (see ICP-OES results below), or simply due to incomplete recovery of the catalyst materials over several cycles. Importantly, the robust nature of the UiO-67 platform allowed the photocatalyst to be highly stable even under the mildly basic reaction conditions required (as confirmed by PXRD, Fig. S6). ^{1}H NMR showed that there is minimal leaching of the Ru complex from the MOF after one catalytic run (Fig. S7; although a small degree of dcbp^{2-} ligand was observed in the reaction solution, Fig. S8). After 5 cycles, inductively coupled plasma-optical emission spectroscopy (ICP-OES) confirmed an atomic ratio of 1:0.106 (Zr/Ru), ~10% lower than fresh UiO-67-[Ru(bpy)$_3$]$_{0.1}$ which gave an atomic ratio of 1:0.118 (Zr/Ru).

Table 1. Summary of results for the aerobic oxidative hydroxylation of arylboronic acids using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst.[a]



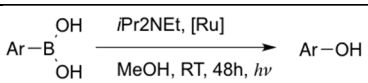
Entry	Catalyst	Light	Atmosphere	Yield (%)[b]	Yield (%)[c]
1	UiO-67-[Ru(bpy)$_3$]$_{0.1}$	+	Air	81(7)	77(3)
2	Ru(bpy)$_3$Cl$_2$	+	Air	>95	>95
3	UiO-67-bpy$_{0.25}$	+	Air	22(2)	0
4	None	+	Air	0	0
5	UiO-67-[Ru(bpy)$_3$]$_{0.1}$	−	Air	0	0
6	UiO-67-[Ru(bpy)$_3$]$_{0.1}$	+	N_2	0	0

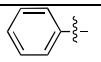
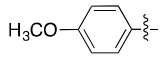
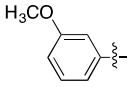
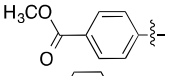
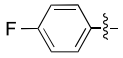
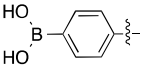
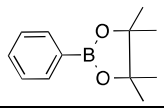
[a] Reaction conditions: phenylboronic acid (0.5 mmol), *N,N*-diisopropylethylamine (0.6 mmol), UiO-67-[Ru(bpy)$_3$]$_{0.1}$ = [Ru] (5 mol%) in 5 mL MeOH open to air with light irradiation at room temperature for 24 h. [b] λ = 365 nm. [c] 23W compact fluorescent bulb. [b,c] Yield is based on ^{1}HNMR analysis.

The scope of near-UV and visible light-induced photocatalytic aerobic oxidative hydroxylation of arylboronic acids is summarized in Table 2 (Fig. S9-S11). The majority of substrates were oxidized to aryl alcohols in good to excellent yields, with conversions under irradiation with visible light or UV light being very similar. The slightly lower yields with visible light are likely due to the weaker visible-light source. A higher conversion efficiency was observed when treating with electron-rich arylboronic acids (Table 2, Entry 2-4). (4-Flurophenyl)boronic acid (Table 2, Entry 5) shows lower yield, which is consistent with homogeneous system.[26] 1,4-Phenylenediboronic acid also proved to be suitable substrate for this reaction, but with a lower conversion (~20%) for the double oxidation (Fig. S12). Increasing amount of catalyst and sacrificial agents (*i*Pr$_2$NEt) and using pure O_2 instead of air could potentially enhance the yield of these reactions.[26] Finally, the substrate scope was extended to the use of phenylboronic acid pinacol ester (Table 2, Entry 7), which is a derivative of phenylboronic acid. The yield for this substrate was >90% under both near-UV and visible-light irradiation (Fig S13).

In conclusion, an example of a heterogeneous photocatalyst for the aerobic oxidative hydroxylation of arylboronic acids was prepared by incorporating polypyridyl ruthenium complexes into a UiO-67 MOF via a combination of using a mixed ligand MOF with PSM. The synthesized UiO-67-[Ru(bpy)$_3$]$_{0.1}$ photocatalyst is stable and active over several cycles, providing a platform to recover and reuse this precious metal-containing catalyst.

Table 2. Scope of substrate conversion using UiO-67-[Ru(bpy)$_3$]$_{0.1}$ as catalyst.



Entry	Ar-	Yield (%)[a]	Yield (%)[b]
1		81(7)	80(5)
2		74(2)	72(2)
3		76 (3)	70(2)
4		>95	>95
5		50 (5)	47(3)
6		20 (3)	15(2)
7		>95	91(1)

[a] λ = 365 nm. [b] 23W compact fluorescent bulb. [a, b] Yield determined by ^{1}H NMR from three independent experiments.

This work was supported by a grant from the Division of Chemistry of the National Science Foundation (CHE-1359906). We thank Dr. H. Fei (UCSD) for assistance with PXRD and ^{1}HNMR analysis, Dr. Y. Su (UCSD) for assistance with mass spectrometry experiments, Dr. Z. Zhang (UCSD) for assistance with gas adsorption test, and H. Liu (UCSD) for assistance with ICP-OES measurements.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of synthesis and catalysis, additional characterization. See DOI: 10.1039/c000000x/

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