Postsynthetic Metalation of Bipyridyl-Containing Metal−Organic Frameworks for Highly Efficient Catalytic Organic Transformations

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S *Supporting Information*

ABSTRACT: We have designed highly stable and recyclable single-site solid catalysts via postsynthetic metalation of the 2,2′-bipyridyl-derived metal−organic framework (MOF) of the UiO structure (bpy-UiO). The Ir-functionalized MOF (bpy-UiO-Ir) is a highly active catalyst for both borylation of aromatic C−H bonds using $B_2(pin)_2$ (pin = pinacolate) and *ortho*-silylation of benzylicsilyl ethers; the *ortho*-silylation activity of the bpy-UiO-Ir is at least 3 orders of magnitude higher than that of the homogeneous control. The Pd-functionalized MOF (bpy-UiO-Pd) catalyzes the dehydrogenation of substituted cyclohexenones to afford phenol derivatives with oxygen as the oxidant. Most impressively, the bpy-UiO-Ir was recycled and reused 20 times for the borylation reaction without loss of catalytic activity or MOF crystallinity. This work highlights the opportunity in designing highly stable and active catalysts based on MOFs containing nitrogen donor ligands for important organic transformations.

Chelating ligands containing pyridyl moieties such as bipyridines, phenanthrolines, and terpyridines are extensively used ligand frameworks in coordination chemistry and homogeneous catalysis.[1−4] Owing to their robust redox stability, coordinating ability with a wide range of metal ions, and the ease of functionalization, these pyridyl ligands have offered an interesting alternative to phosphine-based ligands in developing catalytic systems for fine chemical synthesis.[5−8] Nevertheless, homogeneous catalysts based on nitrogen donor ligands tend to have more open coordination environments than their phosphine counterparts and are thus more prone to deactivation via intermolecular pathways. Moreover, homogeneous catalysts based on rigid nitrogen donor ligands can have poor solubility in typically nonpolar solvents used in many catalytic reactions. Immobilization of homogeneous catalysts and isolation of catalytic sites using a solid support provide an interesting approach to circumvent these potential problems.

In this context, metal−organic frameworks (MOFs) have attracted increasing interest in recent years as a new class of porous molecular materials for various potential applications.[9−16] In particular, MOFs have provided a highly tunable platform for designing single-site solid catalysts for a variety of useful organic transformations.[17−24] Importantly, MOFs and related cross-linked polymers were shown to stabilize highly active species that could undergo bimolecular deactivation in solution.[25−27] We have been particularly interested in developing highly efficient single-site solid catalysts based on UiO-type MOFs because of their stability under a range of reaction conditions.[25] First reported by Lillerud et al. in 2008,[28,29] the UiO series of MOFs are built from $Zr_6O_4(OH)_4(O_2CR)_{12}$ secondary building units (SBUs) and linear dicarboxylate bridging ligands and have allowed for the design of novel functional materials by incorporating a wide variety of functionalities into the dicarboxylate bridging ligands. Herein, we report the UiO-type MOF with the 2,2′-bipyridyl moiety (bpy-UiO) as an orthogonal functional fragment and its postsynthetic metalation to afford highly robust and active solid catalysts for a broad scope of organic reactions.[30,31]

Bpy-UiO was synthesized via a solvothermal reaction between $ZrCl_4$ and 2,2′-bipyridine-5,5′-dicarboxylic acid in the presence of DMF and trifluoroacetic acid. The resulting solid showed an identical powder pattern to that simulated from the single crystal structure (Figure 1a, 1d).[31a] Bpy-UiO exhibited a BET surface area of 2277 m^2/g and a pore size of 7.2 Å, consistent with the single crystal structure (Figures S1 and S2, Supporting Information [SI]). The postsynthetic metalation of bpy-UiO was performed by treating bpy-UiO with 2.0 equiv of [Ir(COD)(OMe)]$_2$ in THF to afford bpy-UiO-Ir as a deep green solid or with 4.0 equiv of [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ in DMSO to afford bpy-UiO-Pd as a light yellow solid.[32,33] The crystallinity of bpy-UiO was maintained in both bpy-UiO-Ir and bpy-UiO-Pd as shown by their PXRD patterns that are the same as that of bpy-UiO (Figure 1d and 1e). Inductively coupled plasma-mass spectrometry (ICP-MS) analyses of Zr/Ir and Zr/Pd ratios of the digested metalated MOFs provided Ir and Pd loadings of 30% and 24% for bpy-UiO-Ir and bpy-UiO-Pd, respectively. Nitrogen adsorption measurements indicated that both bpy-UiO-Ir and bpy-UiO-Pd have much reduced BET surface areas (365.0 and 457.5 m^2/g, respectively) and slightly reduced pore sizes of 5.6 and 6.7 Å, respectively (Figures S2, S5, and S9; SI). The smaller surface areas, pore sizes, and pore volumes of bpy-UiO-Ir and bpy-UiO-Pd are due to the presence of Ir/Pd cations and associated ligands in the MOF cavities. TEM images showed that bpy-UiO has a particle size of ∼300 nm (Figure 1b) and the particles appear to be highly aggregated.

Bpy-UiO-Ir exhibited excellent activity in dehydrogenative borylation of aromatic C−H bonds using $B_2(pin)_2$ (pin = pinacolate) as the borylating agent.[34−36] Borylation of aryl C−H bonds provides aryl boronic esters, which are employed as reagents in many important reactions for synthesizing organic compounds.[37−42] Bpy-UiO-Ir catalyzed borylation reactions
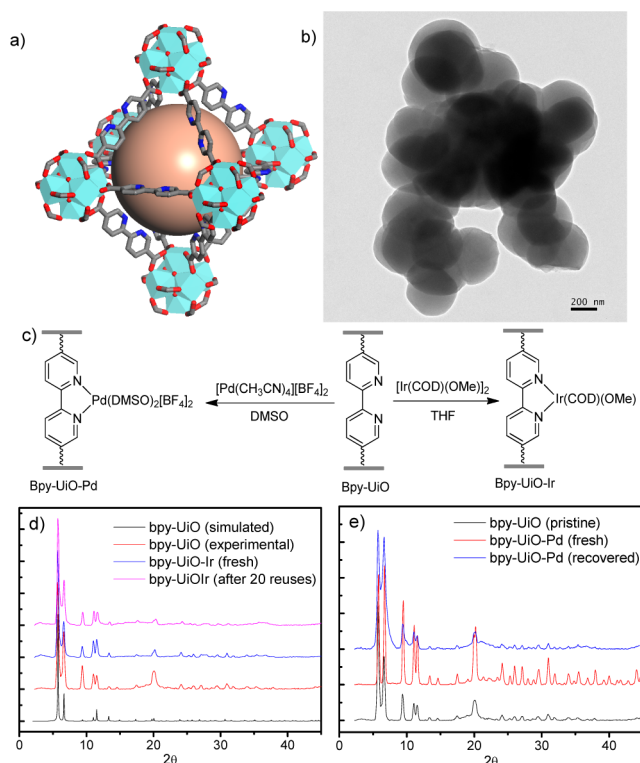
Figure 1. (a) X-ray crystal structure and (b) TEM image of the bpy-UiO MOF. (c) Postsynthetic metalation of bpy-UiO to form bpy-UiO-Ir and bpy-UiO-Pd. (d) PXRD pattern simulated from the CIF file[31a] (black) and PXRD patterns of pristine bpy-UiO (red), freshly prepared bpy-UiO-Ir (blue), and bpy-UiO-Ir recovered from the 21st run of borylation of *m*-xylene (purple). (e) PXRD patterns of pristine bpy-UiO (black), freshly prepared bpy-UiO-Pd (red), and bpy-UiO-Pd recovered from dehydrogenation of 3-methylcyclohex-2-enone (blue).

Table 1. Bpy-UiO-Ir Catalyzed C−H Borylation of Arenes[a]

Entry	Arene	Product	Time	Isolated Yield (%)
1	indole	indole-Bpin	28 h	85
2			4 d	83[b]
3	Br, I benzene	Br, I, Bpin	12 h	86
4	1,2-dimethoxybenzene	dimethoxy-Bpin	10 h	93
5[c]	o-xylene	o-xylene-Bpin	9 h	96
6[c]			4 d	96[b]
7[c]	m-xylene	m-xylene-Bpin	7 h	94
8[c]	1,2-dichlorobenzene	dichloro-Bpin	8 h	93
9[c]			4 d	95[b]
10	1,4-dichlorobenzene	dichloro-Bpin	17 h	91
11[c]	toluene	toluene-Bpin	15 h	93 (o:m:p = 0:60:40)

[a]Reaction conditions: 0.5 mol % bpy-UiO-Ir, 81.9 μmol B₂pin₂, 163.9 μmol of arene, 2.0 mL of heptane, 100 °C. [b]0.1 mol % bpy-UiO-Ir. [c]Neat arene was used.

with B$_2$(pin)$_2$ were first screened in several solvents and in neat arenes (without using a solvent) to obtain the best conditions of 100 °C in heptane or in neat arenes (Table S1, SI). At 0.5 mol % catalyst loading, bpy-UiO-Ir gave complete conversions and afforded the borylated arenes in 85−96% isolated yields (Table 1). MOF-catalyzed borylation reactions have a broad substrate scope, allowing the borylation of a wide range of activated and unactivated arenes, including halogenated-, alkyl-, and alkoxy-arenes. The regioselectivities of the borylated products are the same as those reported for the homogeneous catalysts by functionalizing the α-C centers in heteroarenes and the least sterically hindered carbon centers in unactivated arenes.[36] The C−H borylation of rigid and larger substrates required longer reaction times due to the slower diffusion of substrates and products through the MOF channels (Table 1, entries 1, 3, and 4). Time-dependent GC conversion curves indicated that, in spite of the slower diffusion of reactants through MOF channels than in homogeneous solution, bpy-UiO-Ir was at least twice as active as the homogeneous control [(CO$_2$Me)$_2$bpy]Ir(COD)-(OMe) in terms of turnover frequency (Figure 2a). At 0.5 mol % catalyst loading, the borylation of *m*-xylene was completed in 8 and 17 h for bpy-UiO-Ir and [(CO$_2$Me)$_2$bpy]Ir(COD)(OMe), respectively (Figure 2a). The higher activity of bpy-UiO-Ir is likely due to active site isolation which prevents any intermolecular deactivation pathways.

Remarkably, at a 2 mol % catalyst loading, bpy-UiO-Ir could be recovered and reused for the borylation of *m*-xylene for at least 20 times without significant loss of catalytic activity (Figures 2b and

S14) or MOF crystallinity (Figures 1d and S13). Excellent yields (87−95%) of the borylated product, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene, were obtained consistently in the reuse experiments. B$_2$(pin)$_2$ was completely consumed within 4 h during the first 9 runs, but the reaction took progressively longer time to complete starting from the 13th run (Figure 2b). The reaction took 6 h to complete in the 13th run and 8 h in the 21st run. The slightly longer reaction time needed for the later runs is presumably due to the accidental loss of the MOF catalyst during the workup step (due to the small reaction scale). The bpy-UiO-Ir catalyst thus gives a much higher total turnover number (at least 20 times) as a result of catalyst recycling and reuse. Importantly, the borylation product was obtained in high purity simply by removing the solid catalyst and the organic volatiles. The heterogeneous nature of bpy-UiO-Ir was further confirmed by several experiments. The PXRD patterns of bpy-UiO-Ir recovered from the 5th, 9th, and 21st run remained essentially unchanged from that of freshly prepared bpy-UiO-Ir (Figures 1d and S15), indicating that the MOF catalyst is very stable under the catalytic conditions. Additionally, ICP-MS analyses showed that the amounts of Ir and Zr leaching into the supernatant after the first run were <0.03% and <0.003%, respectively, and the amounts of leached Ir and Zr after the ninth
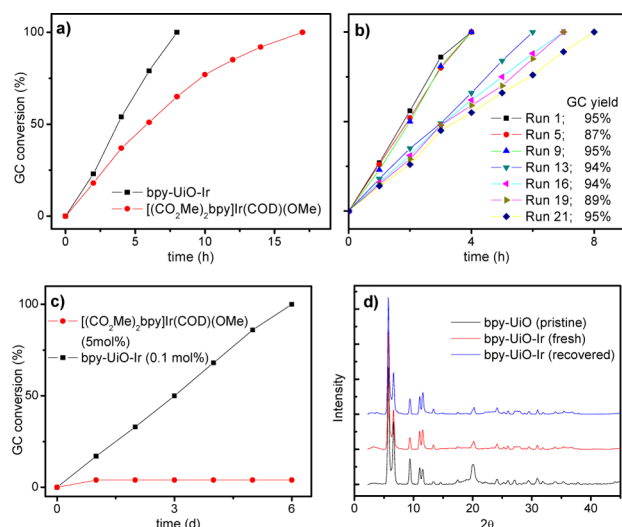
Figure 2. (a) Plots of GC conversion (%) vs time (h) for C−H borylation of *m*-xylene using bpy-UiO-Ir (0.5 mol %) and [(CO₂Me)₂bpy]Ir(COD)(OMe) (0.5 mol %) as catalysts under identical conditions. (b) Plots of GC conversion (%) vs time (h) for various runs in the recycle and reuse of bpy-UiO-Ir for borylation of *m*-xylene. (c) Plots of GC conversion (%) vs time (d) for *ortho*-silylation of **3a** using bpy-UiO-Ir (0.1 mol %) and [(CO₂Me)₂bpy]Ir(COD)(OMe) (5 mol %) as catalysts under identical conditions. (d) PXRD patterns of pristine bpy-UiO (black), freshly prepared bpy-UiO-Ir (red), and bpy-UiO-Ir recovered from *ortho*-silylation of **3a** (blue).

run were <0.01% and <0.001%, respectively. Moreover, no further conversion was detected after removal of bpy-UiO-Ir during the course of the borylation reaction (Scheme S2).

Bpy-UiO-Ir is also active in catalyzing intramolecular *ortho*-silylation of benzylicsilyl ethers to give benzoxasiloles (Table 2).[6,43] Benzoxasiloles are important in organic synthesis and can be converted to phenol by Tamao−Fleming oxidation[44] or to biaryl derivatives by Hiyama cross-coupling reactions.[45] Screening experiments of solvents and reaction conditions revealed that the silylation reaction gave the highest turnover frequency when performed in *n*-heptane at 100 °C (Table S2, SI). At 1.0 mol % catalyst loading and under these optimized conditions, bpy-UiO-Ir provided benzoxasiloles (**4a−4e**) in good isolated yields (83−94%). Importantly, no H-acceptor is needed for the silylation reaction, which is a significant improvement over the corresponding homogeneous silylation reaction in terms of atom efficiency. The catalyst loading could be decreased to 0.1 mol % albeit at the cost of increasing the reaction time from 30 h to 6 days (entries 2 and 4, Table 2). Additionally, longer reaction times were required for larger substrates, presumably because of the slower substrate diffusion through the MOF channels (Table 2, entries 5−7). Notably, the homogeneous control [(CO₂Me)₂-bpy]Ir(COD)(OMe) had a very low activity for the silylation reaction. Under identical conditions, 5.0 mol % of [(CO₂Me)₂-bpy]Ir(COD)(OMe) afforded **4a** in only 4% conversion in a day, after which no further conversion was observed with prolonged heating. In contrast, the conversion of **4a** proceeded linearly with time until completion in the presence of at 0.1 mol % of the bpy-UiO-Ir catalyst (Figure 2c). This result indicates that bpy-UiO-Ir is at least 1250 times more active than the homogeneous control for the silylation reaction, strongly supporting the beneficial effect of active site isolation in an MOF catalyst. The PXRD of bpy-UiO-Ir recovered from the silylation reaction remained the same as that of freshly prepared bpy-UiO-Ir (Figure 2d). Bpy-

Table 2. Bpy-UiO-Ir Catalyzed Intramolecular *ortho*-Silylation of Benzylicsilyl Ethers to Benzoxasiloles[a]

entry	R¹	R²	time	yield[b]
1	H	Me	30 h	94
2	H	Me	6 d	90[c]
3	Me	Me	30 h	92
4	Me	Me	6 d	91[c]
5	OMe	Me	50 h	85
6	Cl	Me	44 h	92
7	H	Ph	72 h	83

[a]Reaction conditions: 1.0 mol % bpy-UiO-Ir, 2.0 mL of *n*-heptane, 100 °C. [b]Isolated yield. [c]0.1 mol % bpy-UiO-Ir.

Table 3. Bpy-UiO-Pd Catalyzed Dehydrogenation of Substituted Cyclohexenones to Phenols[a]

entry	R	solvent	temp (°C)	time	conv (%)[b,c]
1	H	toluene	80	3 d	80
2	H	DMSO	80	55 h	100
3	H	*m*-xylene	100	3 d	39
4	H	DMSO	100	32 h	100 (93)
5	H	DMF	100	3 d	82
6	Me	DMSO	100	35 h	100 (86)
7	Et	DMSO	100	44 h	100 (91)
8	Ph	DMSO	100	70 h	100 (83)

[a]Reaction conditions: 1.0 mol % bpy-UiO-Pd. [b]Conversions were determined by GC. [c]Isolated yield in the parentheses.

UiO-Ir is thus a robust, reusable, and active single-site solid catalyst for important organic transformations.

We next examined the applicability of bpy-UiO in other metal catalyzed reactions. We turned our attention to the catalytic activity of bpy-UiO-Pd because [(6,6′-dmbpy)Pd(CH₃CN)₄]-[BF₄]₂ (6,6′-dmbpy = 6,6′-dimethyl-2,2′-bipyridine) was recently shown by Stahl et al. to be a highly active catalyst for dehydrogenation of substituted cyclohexenones.[46,47] Bpy-UiO-Pd is active in the dehydrogenation of substituted cyclohexenones to phenol under 1 atm of O₂. The reaction conditions were optimized by monitoring the conversion of cyclohexenone to phenol (**6a**) with 1.0 mol % bpy-UiO-Pd by GC analysis. Phenol could be obtained in moderate yields (39−80%) in DMF and aromatic solvents such as toluene and *m*-xylene at 80−100 °C. The highest yield (93%) was obtained when the reaction was performed in DMSO at 100 °C. However, the yield of phenol dropped significantly in DMSO at 120 °C even though the MOF catalyst remained crystalline (Figure S16), presumably due to the decomposition of the bpy-UiO-Pd catalyst. Under 1 atm of O₂, 1.0 mol % bpy-UiO-Pd afforded 3-substituted phenols **6b**, **6c**, and **6d** (entries 6−8, Table 3) in DMSO at 100 °C in 83−91% isolated yields. Bpy-UiO-Pd also compares favorably to its homogeneous counterpart, with at least three times as high activity as the homogeneous control. The homogeneous catalyst [{(CO₂Me)₂bpy}Pd(CH₃CN)₄][BF₄]₂ that was prepared in situ from (CO₂Me)₂bpy and [Pd(CH₃CN)₄][BF₄]₂ (1:1 equiv; 3

mol % Pd) afforded phenol quantitatively from cyclohexenone in 36 h in DMSO at 100 °C. During the course of this reaction, a black precipitate formed due to the degradation of the catalyst. After removal of all the volatiles in vacuo, the remaining residue from the homogeneous reaction did not exhibit any catalytic activity for the dehydrogenation of cyclohexenone. In contrast, bpy-UiO-Pd was recycled and reused twice in this reaction (first run, 93%; second run, 91%; third run, 79%). The bpy-UiO-Pd catalyst recovered from the dehydrogenation showed the same PXRD pattern as the as-prepared bpy-UiO-Pd (Figure 1e), indicating that the bpy-UiO-Pd catalyst is stable under the catalytic conditions.

In summary, we have developed a straightforward post-synthetic metalation strategy to prepare highly active single-site solid catalysts based on a UiO-type MOF bearing the bipyridyl moiety. The bpy-UiO-Ir and bpy-UiO-Pd catalysts not only show much enhanced (up to at least 1250 times) catalytic activities compared to their homogeneous analogues but also exhibit higher stability and can be readily reused for a broad scope of important organic transformations. Our current work is focused on extending this method to develop other bpy-UiO based transition metal catalysts that can potentially be used in the practical synthesis of fine chemicals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental section; synthesis and characterization of MOFs; procedures for catalytic reactions; GC analysis conditions for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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