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Impact of Linker Engineering on the Catalytic Activity of Metal–Organic Frameworks Containing Pd(II)–Bipyridine Complexes

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Abstract

A series of mixed-linker bipyridyl metal–organic framework (MOF)-supported palladium(II) catalysts were used to elucidate the electronic and steric effects of linker substitution on the activity of these catalysts in the context of Suzuki–Miyaura cross-coupling reactions. m-6,6'-Me₂bpy-MOF-PdCl₂ exhibited 110- and 496-fold enhancements in activity compared to nonfunctionalized m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂, respectively. This result clearly demonstrates that the stereoelectronic properties of metal-binding linker units are critical to the activity of single-site organometallic catalysts in MOFs and highlights the importance of linker engineering in the design and development of efficient MOF catalysts.

Keywords

bipyridyl linker, heterogeneous catalysis, isorecticular metal–organic frameworks, single-site catalyst, structure–activity relationship, Suzuki–Miyaura cross-coupling

Disciplines

Catalysis and Reaction Engineering | Materials Chemistry

Comments

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Impact of Linker Engineering on the Catalytic Activity of Metal–Organic Frameworks Containing Pd(II)-Bipyridine Complexes

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ABSTRACT: A series of mixed-linker bipyridyl MOF-supported palladium (II) catalysts were used to elucidate the electronic and steric effects of linker substitution on the activity of these catalysts in the context of Suzuki–Miyaura cross-coupling reactions. m-6,6'-Me₂bpy-MOF-PdCl₂ exhibited a 110-fold and 496-fold enhancement in the activity compared to non-functionalized m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂. This result clearly demonstrates that the stereoelectronic properties of metal-binding linker units are critical to the activity of single-site organometallic catalysts in MOFs and highlights the importance of linker engineering in the design and development of efficient MOF catalysts.

KEYWORDS: *isoreticular metal-organic frameworks, single-site catalyst, heterogeneous catalysis, bipyridyl linker, structure–activity relationship, Suzuki-Miyaura cross-coupling.*

In palladium-catalyzed cross-coupling reactions, the steric and electronic properties of ancillary ligands bound to the metal center significantly impact the catalytic properties of palladium complexes.¹ Previous studies detail how the steric and electronic properties of phosphine,² *N*-heterocyclic carbene,^{3,4} and Schiff base⁵ ligands impact palladium-catalyzed Suzuki-Miyaura reactions. However, these studies are primarily limited to homogeneous catalyst systems, and analogous studies on heterogeneous palladium catalysts have rarely been reported.⁶ The lack of systematic studies on the impact of ancillary ligands on heterogeneous palladium catalysts likely results from a lack of catalyst supports that enable facile tuning of ligand structures at the atomic level.

Metal-organic frameworks (MOFs) have recently gained attention due to their high surface area and porosity, structural tunability, as well as applications in diverse areas such as catalysis, chemical sensors, drug delivery, gas storage and separation.⁷⁻¹³ Of particular importance to our studies, MOFs have been established as a versatile platform for the immobilization of homogeneous organometallic catalysts. These catalytic entities are attractive because they integrate the benefits of the well-defined stereoelectronic properties of homogeneous organometallic catalysts with the uniform active sites and recyclability of MOFs. Recent studies have greatly expanded the types of organometallic transformations catalyzed by metalated bipyridyl-MOFs.¹⁴⁻²⁰ However, there remains minimal understanding of how the steric and electronic properties of the bipyridyl linker unit impact the properties of these heterogeneous catalysts.

In comparison to conventional porous supports, MOFs feature the advantages of adjustable pore structures and broad synthetic diversity accessible through an array of structural building units. In addition, MOFs are well suited to establishing clear structure-function relationships through rational

functionalization of linkers in isoreticular MOFs.²¹⁻²⁵ Recent studies have investigated how the identity of linker units in MOFs impacts heterogeneous catalysis.²⁶⁻³⁰ The steric and electronic properties of ancillary ligands are crucial to improving activity in cross-coupling reactions promoted by homogeneous palladium complexes.^{31,32} We envisioned that anchoring homogeneous palladium catalysts in MOFs may allow the heterogeneous catalytic behavior to be fine-tuned in a similar fashion to ligand modification in homogeneous catalyst systems. To the best of our knowledge, studies to elucidate the effects of metal-binding linker units in MOFs on palladium-catalyzed Suzuki-Miyaura cross-coupling have not been reported.

Herein we report the immobilization of palladium chloride within a series of bipyridyl-MOFs (m-bpy-MOF-PdCl₂, m-6,6'-Me₂bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂) synthesized via a mixed-linker approach to afford heterogeneous catalysts for Suzuki-Miyaura cross-coupling reactions (Figure 1). Mixed-linker MOFs (m-MOFs) hold multiple advantages. They possess high surface areas and stability. The bipyridine sites are capable of coordinating palladium complexes,³³⁻³⁶ and the linkers without bipyridine sites facilitate the separation of the active palladium centers in MOFs, preventing deactivation by dimerization of the palladium catalysts.^{14,37} These metalated isoreticular MOFs are crystalline, porous and robust. Importantly, m-6,6'-Me₂bpy-MOF-PdCl₂ exhibited a 110-fold and 496-fold enhancement in the catalytic activity in Suzuki-Miyaura cross-coupling reactions of iodobenzene compared to m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂. m-6,6'-Me₂bpy-MOF-PdCl₂ also exhibited the highest activity and remarkable enhancement in activity for the Suzuki-Miyaura cross-coupling reactions of bromobenzene. This work constitutes the first example detailing the systemat-

ic study of the stereoelectronic properties of ancillary ligands on organometallic catalysis in MOFs.

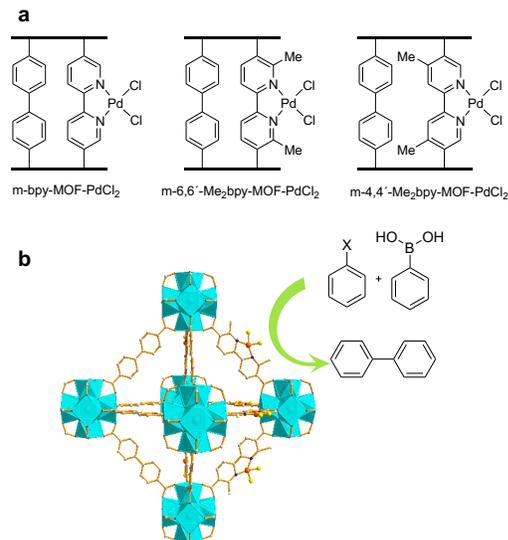


Figure 1. a) Schematic structures of m-MOF-PdCl₂ precatalysts. b) Idealized structure of m-6,6'-Me₂bpy-MOF-PdCl₂ as a precatalyst for the model Suzuki-Miyaura cross-coupling reaction.

At the outset of our studies, we synthesized a series of 2,2'-bipyridine-5,5'-dicarboxylic acid derivatives. 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) was prepared according to a literature procedure.³⁸ The novel 6,6'-dimethyl-[2,2'-bipyridine]-5,5'-dicarboxylic acid (H₂-6,6'-Me₂bpydc) and 4,4'-dimethyl-[2,2'-bipyridine]-5,5'-dicarboxylic acid (H₂-4,4'-Me₂bpydc) derivatives were prepared by a sequence involving nickel-catalyzed reductive homocoupling of ethyl 6-chloro-2-methylnicotinate and methyl 6-chloro-4-methylnicotinate,³⁹ respectively, and subsequent hydrolysis of the resulting diesters. Using this series of bipyridyl linkers, we prepared mixed-linker MOFs (m-bpy-MOF, m-6,6'-Me₂bpy-MOF, and m-4,4'-Me₂bpy-MOF) from equimolar amounts of the bipyridyl and biphenyl linkers (Figure 2a).¹⁶ Powder X-ray diffraction (PXRD) patterns of the MOFs are in good agreement with simulated patterns for UiO-67, indicating that these MOFs have isorecticular crystalline structures (Figure S1). Linker ratios were quantified by ¹H NMR spectroscopy upon digestion of the MOF with HF in d₆-DMSO (Figure S2). m-bpy-MOF, m-6,6'-Me₂bpy-MOF, and m-4,4'-Me₂bpy-MOF contained 52%, 42%, and 43% of the bipyridyl linkers, respectively (Table S1).

The m-MOF-PdCl₂ precatalysts were synthesized by postsynthetic metalation of the mixed-linker MOFs with PdCl₂(CH₃CN)₂ in acetonitrile. PXRD analyses of the metalated MOFs show that the m-MOF-PdCl₂ complexes remain crystalline during the post-synthetic metalation (Figure 2b). We determined the loading of palladium in the metalated MOFs by inductively coupled plasma-mass spectroscopy (ICP-MS). The palladium loadings are 2.8 wt.% for m-bpy-MOF-PdCl₂, 2.9 wt.% for m-6,6'-Me₂bpy-MOF-PdCl₂, and 3.0 wt.% for m-4,4'-Me₂bpy-MOF-PdCl₂. These loadings are con-

sistent with palladium coordination to 19.3%, 25.8% and 26.7% of the total bipyridine sites in m-bpy-MOF-PdCl₂, m-6,6'-Me₂bpy-MOF-PdCl₂, and m-4,4'-Me₂bpy-MOF-PdCl₂.

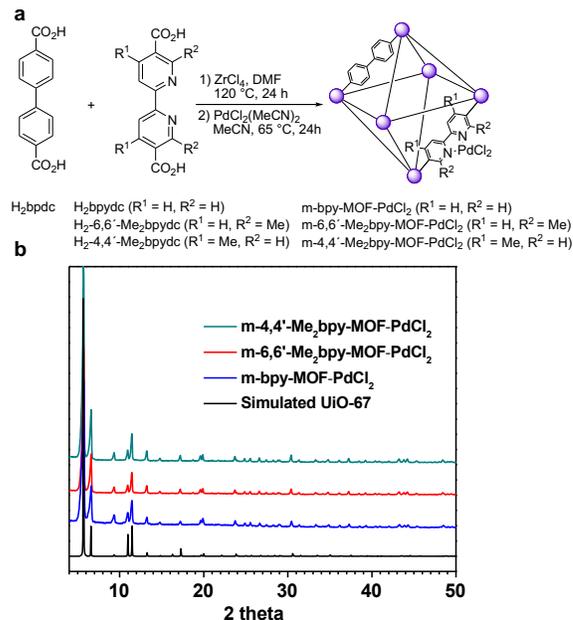


Figure 2. a) Hydrothermal synthesis of m-MOFs; b) PXRD of simulated UiO-67 and m-MOFs-PdCl₂.

N₂ adsorption-desorption isotherm profiles of mixed-linker MOFs and m-MOF-PdCl₂ complexes all exhibit a type I curve, which is characteristic of microporous materials (Figure S3). The Brunauer-Emmett-Teller (BET) surface area and micropore volume of m-bpy-MOF are calculated to be 2600 m² g⁻¹ and 0.91 m³ g⁻¹ (Figure S4), which are in close agreement with reported values (Table S2).¹⁶ The introduction of methyl groups at the 4,4' or 6,6' positions of the bipyridyl linker leads to a decrease in the BET surface areas of the corresponding mixed-linker MOFs. The surface areas of m-6,6'-Me₂bpy-MOF and m-4,4'-Me₂bpy-MOF are 2300 and 2200 m² g⁻¹. The BET surface areas of m-bpy-MOF-PdCl₂, m-6,6'-Me₂bpy-MOF-PdCl₂, and m-4,4'-Me₂bpy-MOF-PdCl₂ decrease to 2300, 2100, and 1900 m² g⁻¹, primarily due to incorporation of PdCl₂ into the cages of the MOFs.

We chose the coupling of iodobenzene with phenylboronic acid as a model reaction to evaluate the effect of linker substitution in Suzuki-Miyaura reactions catalyzed by m-MOFs-PdCl₂ (Figure 3a). During our initial identification of reaction conditions, a range of common solvent and base combinations for Suzuki-Miyaura reactions, including DMF/H₂O (1:1), EtOH/H₂O (1:1), toluene/H₂O (9:1), EtOH, EtOH/H₂O (1:1) with either potassium carbonate or potassium fluoride as the base, were evaluated. However, the metalated MOFs collapsed within 4 hours in the presence of these polar, protic reaction media. Decomposition of the metalated MOFs is not observed when the model coupling reaction is run in toluene with K₂CO₃ as the base. The PXRD and N₂ sorption analyses of the recovered catalysts showed that the crystalline integrity and high surface area of the bpy-UiO MOFs was retained after

the catalysis (Figure S5, Figure S6 and Table S2), indicating the robust nature of the palladium-doped MOF catalysts.

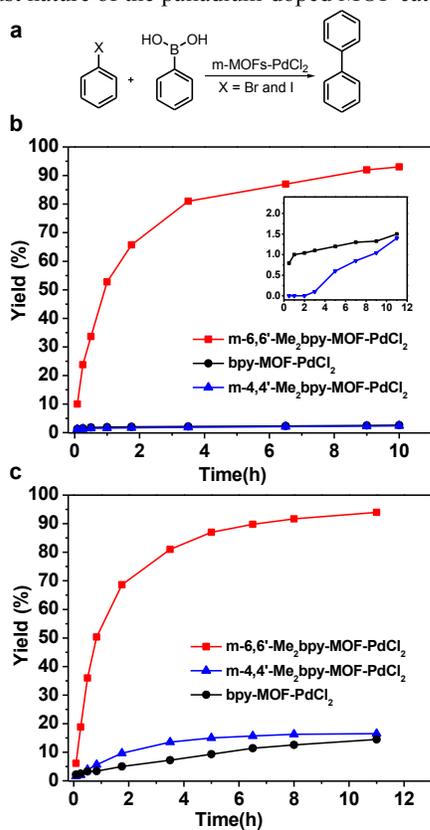


Figure 3. a) Suzuki-Miyaura cross-coupling reaction catalyzed by m-MOF-PdCl₂; b) Catalytic difference of m-MOF-PdCl₂ in coupling reaction of iodobenzene. The inset shows the reaction yield by m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂; c) Catalytic difference of m-MOF-PdCl₂ in coupling reaction of bromobenzene. Reaction conditions: Aryl halide (0.1 mmol), phenylboronic acid (0.15 mmol), K₂CO₃ (0.2 mmol), Toluene (0.5 mL), m-MOF-PdCl₂ (1.0 mol% Pd), Ar atmosphere, 85 °C.

m-bpy-MOF-PdCl₂, m-4,4'-Me₂bpy-MOF-PdCl₂, and m-6,6'-Me₂bpy-MOF-PdCl₂ exhibit dramatic differences in their catalytic activity in the model coupling reaction (Figure 3b). Assuming pseudo-first-order kinetics, we calculated the rate constants for the coupling reaction over m-bpy-MOF-PdCl₂, m-4,4'-Me₂bpy-MOF-PdCl₂ and m-6,6'-Me₂bpy-MOF-PdCl₂ to be 0.24 min⁻¹, 0.05 min⁻¹ and 26.3 min⁻¹, respectively. The m-6,6'-Me₂bpy-MOF-PdCl₂ exhibited a remarkable 110-fold and 496-fold enhancement in the activity compared to non-functionalized m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂. In addition, m-6,6'-Me₂bpy-MOF-PdCl₂ exhibited superior activity in comparison to Pd/carbon (Figure S7). m-6,6'-Me₂bpy-MOF-PdCl₂ showed much higher activity than bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ regardless of the Pd loading. Among m-6,6'-Me₂bpy-MOF-PdCl₂ catalysts with different Pd loading, m-6,6'-Me₂bpy-MOF-PdCl₂ with 2.9 and 5.0 wt.% Pd loading showed similar catalytic activities while m-6,6'-Me₂bpy-MOF-PdCl₂ with 1.0 wt.% Pd loading showed slightly inferior activity for Suzuki-Miyaura

cross-coupling reaction when the same amount of Pd (1.0 mol% to substrate) was used in the coupling reaction (Figure S8). The model coupling reaction of iodobenzene with phenylboronic acid in the presence of m-6,6'-Me₂bpy-MOF-PdCl₂ (1.0 mol % palladium relative to iodobenzene) forms biphenyl in 99% yield in 12 h. The m-MOFs without palladium were catalytically inactive, consistent with ligated palladium centers as the active sites for the Suzuki-Miyaura coupling reaction (Table S3, entry 1). It is reported that biphenyl could be synthesized from palladium-catalyzed homocoupling of aryl halides,⁴⁰ or arylboronic acids.⁴¹ To verify the origin of biphenyl product, we conducted the Suzuki-Miyaura coupling reaction of iodobenzene and 4-methylphenylboronic acid with m-6,6'-Me₂bpy-MOF-PdCl₂ under standard reaction conditions and obtained 4-methyl-1,1'-biphenyl as only product (Table S3, entry 2). This result clearly shows that biaryl coupling products are not formed through homocoupling of either the arylboronic acid or the iodoarene coupling partners.

The difference in activity between the metalated mixed-linker MOFs led us to investigate the coupling of bromobenzene with phenylboronic acid in the presence of these catalysts (Figure 3c). As expected, m-6,6'-Me₂bpy-MOF-PdCl₂ displayed the highest activity among the three m-MOF-PdCl₂ catalysts and leads to the formation of biphenyl in 92% yield. However, m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ showed enhanced catalytic activity in coupling of bromobenzene relative to iodobenzene. For example, the reaction of bromobenzene catalyzed by m-4,4'-Me₂bpy-MOF-PdCl₂ forms biphenyl in 17% yield, while the reaction of iodobenzene under otherwise identical reaction conditions forms biphenyl in 3% yield. The low yields of the biaryl product in coupling reactions of iodobenzene catalysed by m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ prompted us to evaluate the potential for a deactivation pathway that is operative with iodobenzene as the electrophile, but not with bromobenzene. We ran the Suzuki-Miyaura coupling reaction of bromobenzene in the presence of iodobenzene (1 equiv.) over m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂. We found the yield of the biaryl product decreased from ca.17% to 2%, indicating that catalysts derived from m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ may be deactivated in couplings of iodobenzene. However, such deactivation was not observed in reactions catalysed by m-6,6'-Me₂bpy-MOF-PdCl₂, demonstrating the importance of linker engineering in the design of transition metal-functionalized MOF catalysts. On the basis of these results, we hypothesize that the identity of the linker plays a key role in preventing catalyst deactivation that requires further studies to elucidate.

Given the fact that the most active m-6,6'-Me₂bpy-MOF-PdCl₂ did not possess either the highest BET surface area or pore volume and all m-MOF-PdCl₂ catalysts exhibited similar pore size distributions (Figure S9), mass transfer/diffusion should not account for the activity difference. Compared to non-functionalized m-bpy-MOF-PdCl₂, m-6,6'-Me₂bpy-MOF-PdCl₂ contains a relatively hindered and electron-rich metal center and is a more active catalyst. We found the activity of m-4,4'-Me₂bpy-MOF-PdCl₂ to be similar to m-bpy-MOF-PdCl₂ in coupling reactions of both iodobenzene and bromobenzene (Figure 3b and 3c), suggesting the electronic character

of the new linker units has minimal impact on the activity of the metalated MOF catalysts. Our data is consistent with reductive elimination, which is favored at sterically congested metal centers, as the turnover-limiting step of the catalytic cycle for this Suzuki-Miyaura coupling reaction.³

We utilized the homogeneous counterparts (PdCl₂ coordinated to the esterified linkers, denoted as 5,5'-(MeO₂C)₂bpy-PdCl₂, 4,4'-Me₂-5,5'-(MeO₂C)₂bpy-PdCl₂, and 6,6'-Me₂-5,5'-(MeO₂C)₂bpy-PdCl₂) as control catalysts for Suzuki-Miyaura reaction. As shown in Figure S10, the homogeneous analog catalysts displayed higher activity. Moreover, the initial slopes indicate that the activity of 6,6'-Me₂-5,5'-(MeO₂C)₂bpy-PdCl₂ is higher than the activities of 5,5'-(MeO₂C)₂bpy-PdCl₂ and 4,4'-Me₂-5,5'-(MeO₂C)₂bpy-PdCl₂. These results are consistent with the relative rates observed for the heterogeneous MOF catalysts, but the rate differences in these homogeneous catalysts are much less.

Since the Suzuki-Miyaura cross-coupling reactions could proceed with a trace amount of a soluble palladium species,⁴² it is important to verify that palladium does not leach from the MOF during catalysis. The heterogeneity of the most active catalyst, m-6,6'-Me₂bpy-MOF-PdCl₂, was assessed by a hot filtration test. We did not observe a further increase in the yield of biphenyl upon the removal of the solid catalyst at 50% conversion (Figure 4a). Moreover, the palladium content in the reaction solution was determined by ICP-MS, and <0.1% of added Pd was detected. These results suggest that the Suzuki-Miyaura cross-coupling reaction in the presence of m-6,6'-Me₂bpy-MOF-PdCl₂ is indeed catalyzed by heterogeneous palladium species. To probe for deactivation of the catalyst under our reaction conditions, we evaluated the reusability of the m-6,6'-Me₂bpy-MOF-PdCl₂ in coupling reactions run to approximately 60% conversion.⁴³ The m-6,6'-Me₂bpy-MOF-PdCl₂ catalyst can be used at least three times without significant decrease in the yield of biphenyl (Figure 4b).

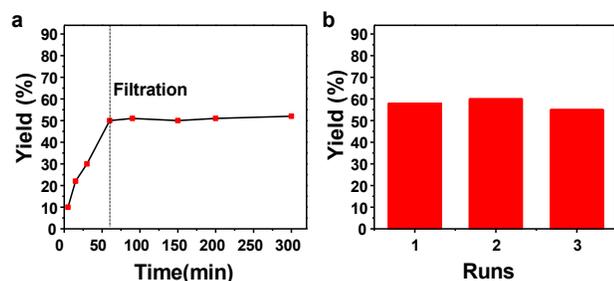


Figure 4. Filtration and recycle test of m-6,6'-Me₂bpy-MOF-PdCl₂ in the Suzuki-Miyaura cross-coupling reaction. Reaction conditions: iodobenzene (0.1 mmol), phenylboronic acid (0.15 mmol), K₂CO₃ (0.2 mmol), Toluene (0.5 mL), m-6,6'-Me₂bpy-MOF-PdCl₂ (1.0 mol% Pd), Ar atmosphere, 85 °C for 1.5 hours.

We have developed a series of functionalized mixed-linker bipyridyl MOF-supported palladium catalysts. We have demonstrated for the first time that simple and systematic modifications to the stereoelectronic properties of linker units in MOFs can significantly impact the activity of metalated MOF catalysts in important organometallic cross-coupling

reactions. m-6,6'-Me₂bpy-MOF-PdCl₂ exhibits dramatically enhanced activity compared to m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ in model Suzuki-Miyaura cross-coupling reactions due to the steric properties at the bpy-palladium sites. m-6,6'-Me₂bpy-MOF-PdCl₂ is also more robust and prevents deactivation pathways observed when m-bpy-MOF-PdCl₂ and m-4,4'-Me₂bpy-MOF-PdCl₂ are used as catalysts of Suzuki-Miyaura cross-coupling reactions of iodobenzene. Control experiments confirm that these reactions proceed through cross-coupling of the haloarene and arylboronic acid without homocoupling of either reaction partner. We showed that the m-6,6'-Me₂bpy-MOF-PdCl₂ is a heterogeneous catalyst of the Suzuki-Miyaura cross-coupling reaction via a hot filtration test and ICP-MS analysis of supernatant solution, and the catalyst can be used three times without obvious deactivation. The present work demonstrates the first systematic example of linker engineering of metalated units in bipyridyl MOFs and highlights the importance of linker design for immobilization of homogeneous catalysts in MOFs. This strategy for linker engineering of metalated units in bipyridyl MOFs for application to additional catalytic organometallic reactions holds great promise and such studies are currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information. PXRD of the catalysts before and after reaction, nitrogen sorption and pore size distribution measurements, ¹H NMR of digested MOFs, synthetic routes to the bipyridyl linkers, and supporting catalytic reaction data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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ABBREVIATIONS

MOFs, metal-organic frameworks; BET, Brunauer–Emmett–Teller; ICP-MS, inductively coupled plasma mass spectroscopy; PXRD, powder X-ray diffraction; m-MOFs, mixed-linker MOFs.

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TOC Figure

