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′-Me_2bpy-MOF-$PdCl_2$ exhibited a 110-fold and 496-fold enhancement in the activity compared to non-functionalized m-bpy-MOF-$PdCl_2$ and m-4,4′-Me_2bpy-MOF-$PdCl_2$. 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 base[5] 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-$PdCl_2$, m-6,6′-Me_2bpy-MOF-$PdCl_2$ and m-4,4′-Me_2bpy-MOF-$PdCl_2$) 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′-Me_2bpy-MOF-$PdCl_2$ 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-$PdCl_2$ and m-4,4′-Me_2bpy-MOF-$PdCl_2$. m-6,6′-Me_2bpy-MOF-$PdCl_2$ 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 systematic study of the stereoelectronic properties of ancillary ligands on organometallic catalysis in MOFs.

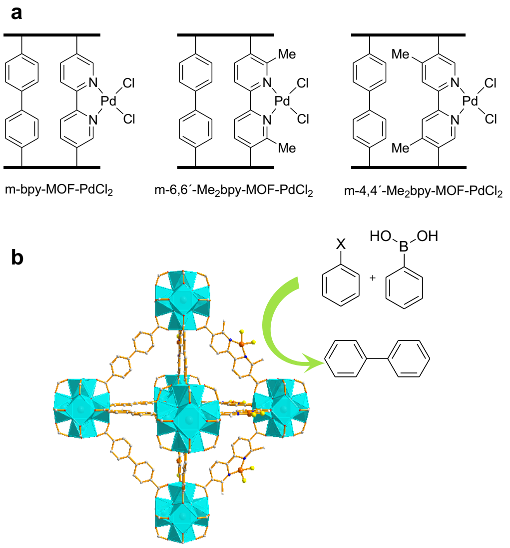

Figure 1. a) Schematic structures of m-MOF-PdCl$_2$ precatalysts. b) Idealized structure of m-6,6′-Me$_2$bpy-MOF-PdCl$_2$ as a precatalyst for the model Suzuki–Miyaura cross-coupling reaction.

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 (H_2bdydc) was prepared according to a literature procedure.[38] The novel 6,6′-dimethyl-[2,2′-bipyridine]-5,5′-dicarboxylic acid (H_2-6,6′-Me$_2$bpydc) and 4,4′-dimethyl-[2,2′-bipyridine]-5,5′-dicarboxylic acid (H_2-4,4′-Me$_2$bpydc) 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′-Me$_2$bpy-MOF, and m-4,4′-Me$_2$bpy-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 isoreticular crystalline structures (Figure S1). Linker ratios were quantified by ^{1}H NMR spectroscopy upon digestion of the MOF with HF in d_6-DMSO (Figure S2). m-bpy-MOF, m-6,6′-Me$_2$bpy-MOF, and m-4,4′-Me$_2$bpy-MOF contained 52%, 42%, and 43% of the bipyridyl linkers, respectively (Table S1).

The m-MOF-PdCl$_2$ precatalysts were synthesized by postsynthetic metalation of the mixed-linker MOFs with $PdCl_2(CH_3CN)_2$ in acetonitrile. PXRD analyses of the metalated MOFs show that the m-MOF-PdCl$_2$ 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-PdCl$_2$, 2.9 wt.% for m-6,6′-Me$_2$bpy-MOF-PdCl$_2$, and 3.0 wt.% for m-4,4′-Me$_2$bpy-MOF-PdCl$_2$. These loadings are consistent with palladium coordination to 19.3%, 25.8% and 26.7% of the total bipyridine sites in m-bpy-MOF-PdCl$_2$, m-6,6′-Me$_2$bpy-MOF-PdCl$_2$, and m-4,4′-Me$_2$bpy-MOF-PdCl$_2$.

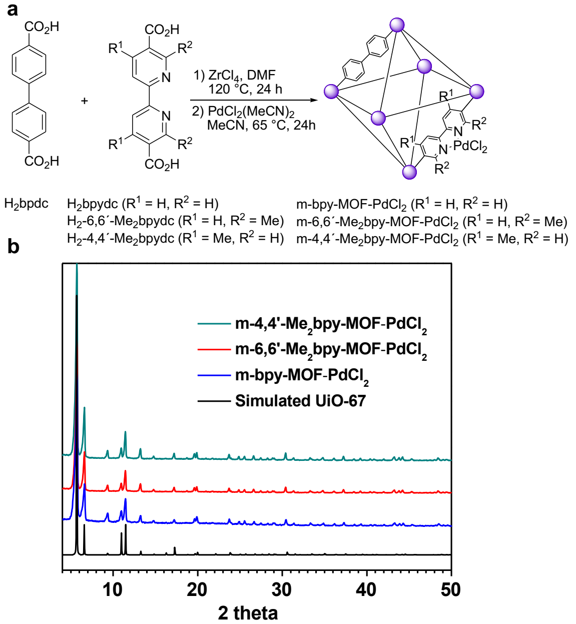

Figure 2. a) Hydrothermal synthesis of m-MOFs; b) PXRD of simulated UiO-67 and m-MOFs-PdCl$_2$.

N_2 adsorption-desorption isotherm profiles of mixed-linker MOFs and m-MOF-PdCl$_2$ 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 m^2 g^{-1} and 0.91 m^3 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′-Me$_2$bpy-MOF and m-4,4′-Me$_2$bpy-MOF are 2300 and 2200 m^2 g^{-1}. The BET surfaces areas of m-bpy-MOF-PdCl$_2$, m-6,6′-Me$_2$bpy-MOF-PdCl$_2$, and m-4,4′-Me$_2$bpy-MOF-PdCl$_2$ decrease to 2300, 2100, and 1900 m^2 g^{-1}, primarily due to incorporation of PdCl$_2$ 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-PdCl$_2$ (Figure 3a). During our initial identification of reaction conditions, a range of common solvent and base combinations for Suzuki-Miyaura reactions, including DMF/H_2O (1:1), EtOH/H_2O (1:1), toluene/H_2O (9:1), EtOH, EtOH/H_2O (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 K_2CO_3 as the base. The PXRD and N_2 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.

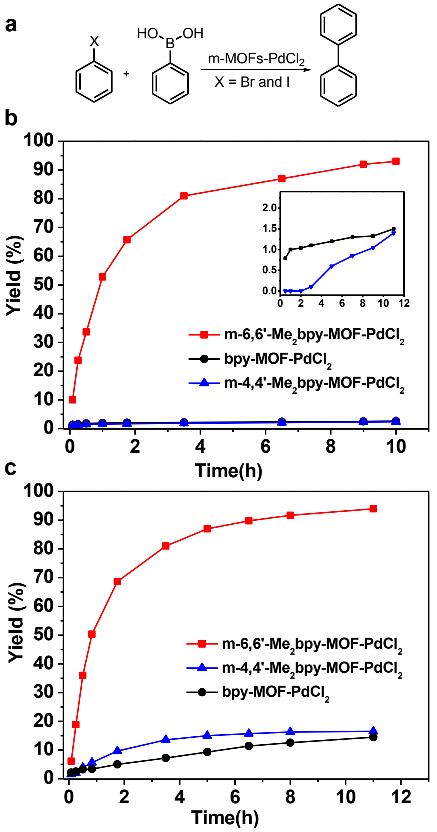

Figure 3. a) Suzuki-Miyaura cross-coupling reaction catalyzed by m-MOF-PdCl$_2$; b) Catalytic difference of m-MOF-PdCl$_2$ in coupling reaction of iodobenzene. The inset shows the reaction yield by m-bpy-MOF-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$.; c) Catalytic difference of m-MOF-PdCl$_2$ in coupling reaction of bromobenzene. Reaction conditions: Aryl halide (0.1 mmol), phenylboronic acid (0.15 mmol), K_2CO_3 (0.2 mmol), Toluene (0.5 mL), m-MOF-PdCl$_2$ (1.0 mol% Pd), Ar atmosphere, 85 °C.

m-bpy-MOF-PdCl$_2$, m-4,4´-Me$_2$bpy-MOF-PdCl$_2$, and m-6,6´-Me$_2$bpy-MOF-PdCl$_2$ 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-PdCl$_2$, m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ and m-6,6´-Me$_2$bpy-MOF-PdCl$_2$ to be 0.24 min^{-1}, 0.05 min^{-1} and 26.3 min^{-1}, respectively. The m-6,6´-Me$_2$bpy-MOF-PdCl$_2$ exhibited a remarkable 110-fold and 496-fold enhancement in the activity compared to non-functionalized m-bpy-MOF-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$. In addition, m-6,6´-Me$_2$bpy-MOF-PdCl$_2$ exhibited superior activity in comparison to Pd/carbon (Figure S7). m-6,6’-Me$_2$bpy-MOF-PdCl$_2$ showed much higher activity than bpy-MOF-PdCl$_2$ and m-4,4’-Me$_2$bpy-MOF-PdCl$_2$ regardless of the Pd loading. Among m-6,6’-Me$_2$bpy-MOF-PdCl$_2$ catalysts with different Pd loading, m-6,6’-Me$_2$bpy-MOF-PdCl$_2$ with 2.9 and 5.0 wt.% Pd loading showed similar catalytic activities while m-6,6’-Me$_2$bpy-MOF-PdCl$_2$ 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´-Me$_2$bpy-MOF-PdCl$_2$ (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´-Me$_2$bpy-MOF-PdCl$_2$ 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´-Me$_2$bpy-MOF-PdCl$_2$ displayed the highest activity among the three m-MOF-PdCl$_2$ catalysts and leads to the formation of biphenyl in 92% yield. However, m-bpy-MOF-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ showed enhanced catalytic activity in coupling of bromobenzene relative to iodobenzene. For example, the reaction of bromobenzene catalyzed by m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ 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-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ 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-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$. We found the yield of the biaryl product decreased from ca.17% to 2%, indicating that catalysts derived from m-bpy-MOF-PdCl$_2$ and m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ may be deactivated in couplings of iodobenzene. However, such deactivation was not observed in reactions catalysed by m-6,6´-Me$_2$bpy-MOF-PdCl$_2$, 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´-Me$_2$bpy-MOF-PdCl$_2$ did not possess either the highest BET surface area or pore volume and all m-MOF-PdCl$_2$ 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-PdCl$_2$, m-6,6´-Me$_2$bpy-MOF-PdCl$_2$ contains a relatively hindered and electron-rich metal center and is a more active catalyst. We found the activity of m-4,4´-Me$_2$bpy-MOF-PdCl$_2$ to be similar to m-bpy-MOF-PdCl$_2$ 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 ($PdCl_2$ coordinated to the esterified linkers, denoted as 5,5´-$(MeO_2C)_2$bpy-$PdCl_2$, 4,4´-Me_2-5,5´-$(MeO_2C)_2$bpy-$PdCl_2$, and 6,6´-Me_2-5,5´-$(MeO_2C)_2$bpy-$PdCl_2$) 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´-Me_2-5,5´-$(MeO_2C)_2$bpy-$PdCl_2$ is higher than the activities of 5,5´-$(MeO_2C)_2$bpy-$PdCl_2$ and 4,4´-Me_2-5,5´-$(MeO_2C)_2$bpy-$PdCl_2$. 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´-Me_2bpy-MOF-$PdCl_2$, 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´-Me_2bpy-MOF-$PdCl_2$ 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´-Me_2bpy-MOF-$PdCl_2$ in coupling reactions run to approximately 60% conversion.[43] The m-6,6´-Me_2bpy-MOF-$PdCl_2$ catalyst can be used at least three times without significant decrease in the yield of biphenyl (Figure 4b).

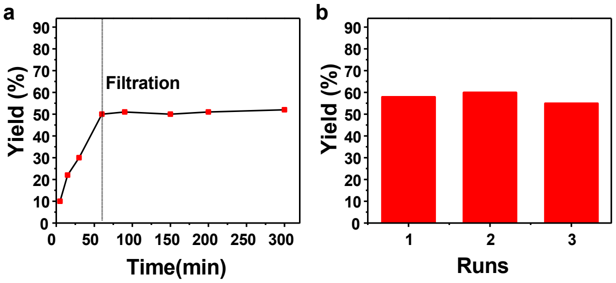

Figure 4. Filtration and recycle test of m-6,6´-Me_2bpy-MOF-$PdCl_2$ in the Suzuki-Miyaura cross-coupling reaction. Reaction conditions: iodobenzene (0.1 mmol), phenylboronic acid (0.15 mmol), K_2CO_3 (0.2 mmol), Toluene (0.5 mL), m-6,6´-Me_2bpy-MOF-$PdCl_2$ (1.0 mol% Pd), Ar atmosphere, 85 °C for 1.5 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´-Me_2bpy-MOF-$PdCl_2$ exhibits dramatically enhanced activity compared to m-bpy-MOF-$PdCl_2$ and m-4,4´-Me_2bpy-MOF-$PdCl_2$ in model Suzuki-Miyaura cross-coupling reactions due to the steric properties at the bpy-palladium sites. m-6,6´-Me_2bpy-MOF-$PdCl_2$ is also more robust and prevents deactivation pathways observed when m-bpy-MOF-$PdCl_2$ and m-4,4´-Me_2bpy-MOF-$PdCl_2$ 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´-Me_2bpy-MOF-$PdCl_2$ 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, ^{1}H 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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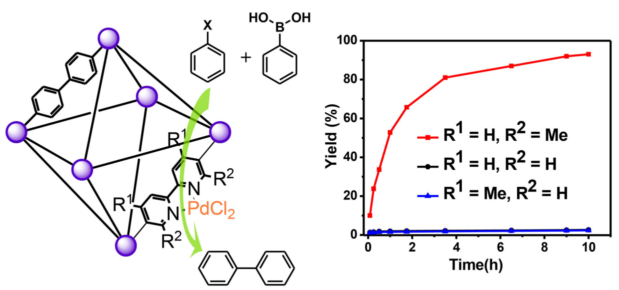
TOC Figure



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