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ARTICLE

Postsynthetic modification of single Pd sites into uncoordinated polypyridine groups of a MOF as the highly efficient catalyst for Heck and Suzuki reactions

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A novel holmium (III) metal-organic framework (Ho-MOF), namely, [Ho(2-TriPP-COO)$_3$] (**2**) had been hydrothermally obtained by using 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (2-TriPP-COOH) and Ho(NO$_3$)$_3$•5H$_2$O and structurally characterized by the single-crystal XRD, powder XRD as well as the elemental analysis. The postsynthetic modification of Ho–MOF was based on the utilization of strong coordination effect between Pd^{2+} ions and the free polypyridine groups at the skeleton of Ho–MOF, which played a critical role to access the highly efficient Pd-HoMOF catalyst. And the Pd-HoMOF exhibited impressively high activity in Heck and Suzuki–Miyaura cross-coupling reactions. Moreover, the MOF catalyst displayed well thermal stability (up to 400 °C), and could be recovered and reused for five reaction cycles. The bridging between MOF structures and homogeneous molecular Pd catalyst could represent a good example in designing highly efficient catalysts for various fine chemical transformations.

Introduction

The development of surface-characterization techniques and advanced synthesis methods have evolved the synthesis of solid catalysts from trial-and-error methodologies into a multidisciplinary science.[1-5] From the global motif of sustainable development in energy and environment area point of view it is vitally important to prepare single metal site catalysts that take full advantage of metal active site, so they have superior reactivity and selectivity.[6-8] As an ideal model combination of homogeneous and heterogeneous catalysis, the performance of catalysts based on single atoms has the high activities of characteristics for the homogeneous catalyst, as well as the advantages of facile separation and recycling.[9-11] To date, the classical synthesis methods for single site catalysts are commonly based on an initial adsorption of metal precursor with a subsequent reduction process.[12] Therefore, the final properties of single site catalysts are highly dependent upon the binding and stabilization of support. To date, some materials such as membranes, organic polymers and inorganic materials have been used as carrier to incorporate noble metal catalysts.[13-17] But very few high density and uniform distribution of single site catalysts were obtained by the traditional anchoring method. Metal-organic frameworks (MOFs), known as hybrid solid materials with periodic network structures built from inorganic connecting points and organic bridging ligands, are crystalline material for which the detailed structures and compositions are known and handled to present the well-defined multiple active sites.[18-34] MOFs thus are particularly attractive candidates of single site heterogeneous catalysts.[35, 36]

Palladium-catalyzed C-C coupling, including Suzuki and Heck reactions, etc. are the reaction of great concern as a versatile route to aryl compounds for pharmaceuticals and fine chemicals.[37] These catalytic reactions usually take place in homogeneous conditions which become difficult reuse of the products and separation of the catalysts after reactions that causes particular economic and environmental concern in large scale synthesis.[38-40] To solve this problem, considerable efforts have been put in the development of heterogeneous catalyst that can be efficiently reused whilst without affecting the inherent activity of the catalytic centers.[41-46] Since one of the extremely serious problem to be overcome in the Pd-based catalysts for fine chemicals and pharmaceuticals is the leaching of palladium from heterogeneous supports/ligand. Accordingly, strategies for introducing coordination bound units in which palladium centers are directly bound to MOFs is

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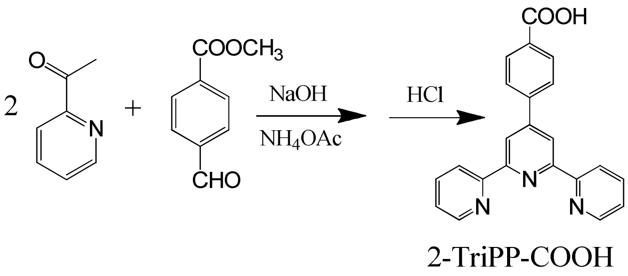
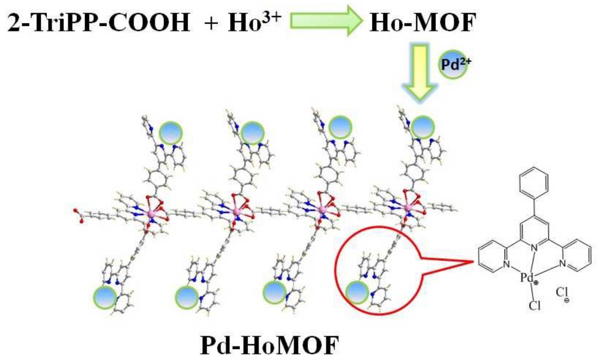
high desirable. Recent reports have showed some examples that post-synthetic modification approach has been applied to incorporate single-site Pd(II) on pre-synthesized MOFs, which is limited typically by the overall stability of the framework under the reaction conditions.[47,48]

Recently, the terpyridine derivatives, as multidentate polypyridine ligands with efficient and stable chelating ability to metal ions, has been intensively explored because of its versatility as building blocks for metal-organic frameworks.[49] Moreover, the terpyridine derivatives have been applied for selective metal ion sensing that can be further used in the creation of some novel optical materials.[50] Besides the integration of terpyridine derivatives into organic polymers, incorporating these functional groups into solid carriers is also an crucial step for the preparation of catalytic materials. For instance, polymer-supported terpyridine palladium complex,[51] silica supported terpyridine palladium(II) complex,[52] terpyridine-functionalized MCM-41 nanoporous silica [53] and the SBA-15-supported iron terpyridine complexes [54] have been used to catalyze alkyl cross-coupling reactions. Herein we wish to describe the synthesis of MOF supported terpyridine palladium(II) complex (Pd–HoMOF, Scheme 1-2) without affecting the integrity of the MOF and demonstrate its catalytic activity in Heck and Suzuki–Miyaura cross-coupling reactions for the high-efficiency activation of C–X bond. Furthermore, the highly active single-site MOF catalyst displayed well thermal stability, negligible Pd(II) cations leaching, and could be recovered and reused for five reaction cycles.



Scheme 1. Schematic representation of the synthetic route for 2-TriPP-COOH ligand.



Scheme 2. Schematic representation of the synthetic route for Pd-HoMOF catalyst. The structure model (down) of Pd-HoMOF shows the incorporation of the palladium(II) ions into the MOF framework. Atomic scheme: holmium, rose; palladium, azure; oxygen, red; nitrogen, blue; carbon, grey.

Experimental section

Materials and general methods

The 2-TriPP-COOH = 4′ -(4-carboxyphenyl)-2,2′ : 6′ ,2″ -terpyridine was synthesized according to procedures described previously.[55] All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were carried out with a PE–2400 elemental analyzer. ^{1}H NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in d^6-DMSO, TMS as internal standard). Pd content of Pd–HoMOF was determined using an inductively coupled plasma (ICP) atomic absorption spectrometer. The leaching amount of Pd–HoMOF in the C-C coupling reactions was determined quantitatively by AAS on the HITACHI Z-2300 instrument. Transmission electron microscopy (TEM; JEOL JEM-2100) were used to acquire the morphology of the catalyst. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB250Xi spectrometer system with an Mg Kα ADES (hν=1253.6 eV) source. IR spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer with KBr pellets in the range 4000–400 cm^{-1}. Powder XRD patterns were obtained using a Bruker D8 ADVANCE XRD diffractometer with CuKα radiation (λ = 1.54056 Å). The thermogravimetric (TG) analysis were performed using a Perkin–Elmer Pyris Diamond TG-DTA thermal analyses system in a nitrogen atmosphere on polycrystalline samples with a heating rate of 20 K min^{-1} from 40 to 800 °C.

Synthesis of 2-TriPP-COOH (1). The 2-acetylpyridine (5.0 g, 41.25 mmol) was added to PEG300 (60 cm^3) containing NaOH (1.65 g, 41.25 mmol), and the suspensions was tirred at 0 ℃ for 15 minutes. 4-(Methoxycarbonyl)benzaldehyde (3.38 g, 20.6 mmol) was then added and the resulting solution was stirred for about 2h at 0 ℃. After 2 h, NH_4OAc (10 g, excess) was added to reaction mixture which was further heated at 100 ℃ for another 2 h. Then the 200 cm^3 water was added reaction mixture and the resultant brown solid crude product 2-TriPP-$COOCH_3$ was collected by filtration, washed two times with 80 cm^3 water, 20 cm^3 cold EtOH (Yield 3.5 g, 48%). Then the 3.5 g 2-TriPP-$COOCH_3$ was added 20 ml HCl (50%) aqueous solution and was heated to 100 ℃ and stirred for 8h. After cooling to room temperature, the precipitate 2-TriPP-COOH was filtered and washed by 30 mL cold EtOH for three times and dried in air (Brown microcrystals, yield 3.22 g, 92%). ^{1}H NMR (400 MHz, DMSO) δ 9.16 – 8.84 (m, 3H), 8.42 (d, J = 6.3 Hz, 1H), 8.19 (q, J = 8.4 Hz, 2H), 7.93 – 7.75 (m, 1H).

Synthesis of [Ho(2-TriPP-COO)$_3$] (2). A mixture of $Ho(NO_3)_3 \bullet 5H_2O$(0.0353 g, 0.1 mmol), 2-TriPP-COOH (0.0441 g, 0.1 mmol) and KOH (0.0224 g, 0.4 mmol) was dissolved in 7 mL distilled water and 3ml DMF with continuous stirring for about

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1h at room temperature. The resulting solution was sealed in a 20 mL stainless steel reactor with a Teflon liner and heated at 120 °C for 3 days under autogenous pressure and then cooled to room temperature, the pink block crystals of 2 were obtained. Yield: 55.2% (based on Ho). Anal. Calcd for $C_{66}H_{42}HoN_9O_6$: C, 64.87; H, 3.46; N, 10.32; Found: C, 64.91; H, 3.49; N, 10.35%; IR (KBr, cm-1): 3479(br), 1609(w), 1598(w), 1582(m), 1560(s), 1549(w), 1521(w), 1463(m), 1427(s), 1411(s), 1262(w), 1163(w), 1116(w), 1092(w), 1070(w), 1039(w), 1017(w), 990(w), 898(w), 862(w), 821(w), 784(m), 738(w), 726(w), 711(w), 704(w), 668(w), 661(w), 639(w), 620(w), 502(w), 482(w), 419(w).

Synthesis of Pd-HoMOF (3). The Pd-HoMOF was sythesized by stirring a mixture of $PdCl_2(CH_3CN)_2$ (285 mg, 1.1 mmol) and [Ho(2-TriPP-COO)$_3$] (Ho-MOF, 611 mg, 0.5 mmol) in dry CH_3CN (10 ml) at 65 °C. After stirring for 24 h, the resulting yellow solid was filtered and washed with CH_3CN. Finally, the Pd-HoMOF was dried at 90 °C for 10 h under vacuum. IR (KBr, cm-1): 3479(br), 1609(w), 1601(w), 1583(m), 1560(s), 1550(w), 1529(w), 1465(m), 1426(s), 1411(s), 1264(w), 1162(w), 1116(w), 1091(w), 1072(w), 1037(w), 1017(w), 989(w), 897(w), 861(w), 819(w), 784(m), 738(w), 727(w), 711(w), 705(w), 668(w), 661(w), 639(w), 620(w), 502(w), 483(w), 419(w).

General Experimental Procedure for the Heck Reaction. The Pd-HoMOF (0.4 mol%) and K_2CO_3 (1.5 mmol) was stirred in DMF (5.0 ml) for 10 min. Then aryl halide (0.5 mmol) and olefin (0.75 mmol) were added and magnetically stirred for an appropriate time (Table 2) at 100 °C. At the end of reaction, the reaction solution was cooled to room temperature and the Pd-HoMOF was separated by filtration. The yields of the crude products were carried out by GC-MS.

General Experimental Procedure for the Suzuki Reaction. The Pd-HoMOF (0.4 mol%) and KOH (1.5 mmol) was stirred in DMF (5.0 ml) for 10 min. Then aryl halide (0.5 mmol) and phenylboronic acid (0.75 mmol) were added and magnetically stirred for an appropriate time (Table 3) at 100 °C. At the end of reaction, the reaction solution was cooled to room temperature and the Pd-HoMOF was separated by filtration. The yields of the crude products were carried out by GC-MS.

Prep-HPLC Separation. Prep-HPLC separation was performed with YMC-C18 column (250 × 10 mm i.d., 5 μm, Shimadzu LC-20AR, Tokyo, Japan) with a solvent of methanol–water (90:10) at a flow rate of 5 mL/min and monitored at 254 nm.

X–ray date collection and structure determination.

Data collection of compound HoMOF was performed on a Bruker AXS Smart APEX II CCD X-diffractometer equipped with graphite monochromated MoKα radiation ((λ = 0.71073 Å) at 293 ± 2K. The structure was solved by direct methods and refined by full matrix least-squares fitting on F^2 by using SHELXS–2014/7.[56] All non–hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. Details of crystallographic data of compounds HoMOF were summarized in Table S1. Selected bond lengths and angles of compounds HoMOF were listed in Table S2.

Results and discussion

By using the 2-TriPP-COOH and $Ho(NO_3)_3{\bullet}5H_2O$, a novel Ho-MOF had been synthesized under hydrothermal conditions. Through postsynthetic modification from the $PdCl_2(CH_3CN)_2$ palladium precursor with of the Ho–MOF, a well-defined palladium metal-organic framework Pd-HoMOF was obtained. The powder XRD patterns for Ho–MOF and Pd-HoMOF, and the simulated XRD patterns of Ho-MOF were shown in the Fig. 1. The diffraction peaks of the powder XRD could be well consistent with simulated XRD patterns, indicating that the title compounds were in the homogeneous phase and the structural integrity after the postsynthetic modification. Inductively coupled plasma mass spectrometry (ICP-MS) experiment with Pd–HoMOF indicated more than 2.51 wt% of the palladium was anchored to Ho-MOF. The TEM experiment was carried out on the Pd–HoMOF to survey the dispersion morphology after incorporating Pd(II) sites into uncoordinated polypyridine groups of MOFs, and the results indicated that there were no distinct aggregation of the Pd particles during the Pd–HoMOF synthesis (Fig. 2a). The C-O bands between 1410 and 1610 cm^{-1} were not changed in the reaction process, which demonstrated the MOF material constructed by Ho ions and carboxylate ligand was preserved in the post-synthetic process (Fig. S1). In addition, the appearance of two peaks (at 477 and 496 cm^{-1}) for Pd–N in IR spectra supported the loading of Pd on Ho-MOF through the palladium–polypyridine complex (Fig. S2).[57] It was further confirmed by the PXRD patterns after the post-synthetic modification. To determine the coordination environment for Pd(II) ions within the materials, we did XPS analysis on Pd–HoMOF (Fig. 3). The results suggested that the material exhibited the Pd 3d$_{5/2}$ band and Pd 3d$_{3/2}$ band at around 338 eV and 343 eV, respectively. These values correspond to the Pd(II) binding energy of Pd–HoMOF. Furthermore, the XPS measurement revealed that the atomic ratio of Cl:Pd is 2:1, which were good agreement with previous studies.[58] Thermogravimetric analysis of the compounds HoMOF and Pd-HoMOF revealed that they are thermally stable up to above 400 °C (Fig. S3, S4), and that demonstrated the high stability of the materials.

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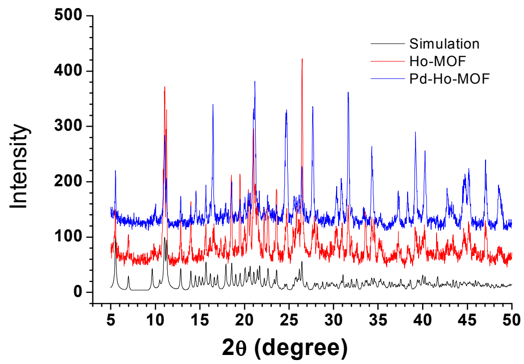


Fig. 1. XRD patterns of the simulated XRD patterns (black line), pre-synthetic Ho-MOF (red line), and the post-synthetic Pd-HoMOF (blue line).

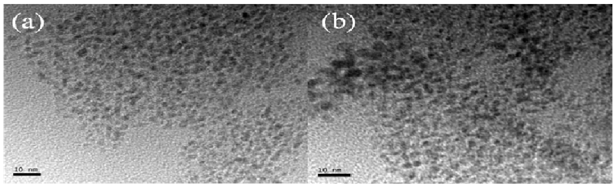


Fig. 2. TEM micrographs of Pd-HoMOF before the reaction (left) and after five catalytic cycles (right).

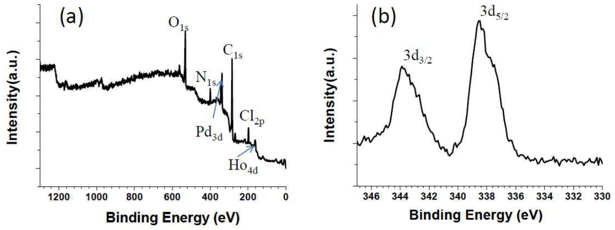


Fig. 3. (a) XPS spectra of Pd-HoMOF; (b) XPS spectra of Pd $3d_{3/2}$ and $3d_{5/2}$ peak positions for Pd-HoMOF.

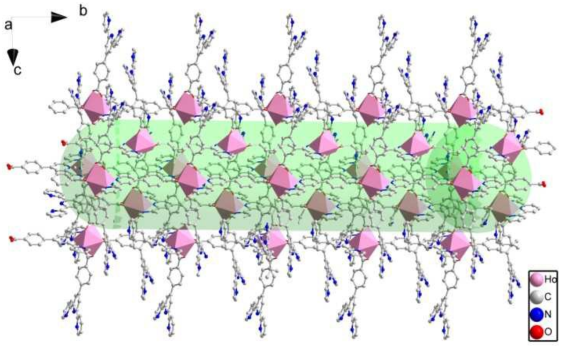
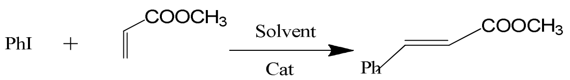


Fig. 4. Polyhedral views of 3D supramolecular framework structures of compound HoMOF in the bc−plane. Pink polyhedra: $\{HoO_6N_3\}$.

Crystal structures of Ho-MOF

Single-crystal XRD analysis revealed that the compound Ho-MOF crystallized in the monoclinic C2/c space group. There were one crystallographically Ho^{3+} ions and three 2-TriPP-COO- ligands in the structure unit (Fig. S5). Each Ho^{3+} ion exhibited nine–coordinated environment that was coordinated by six oxygen atoms from three 2-TriPP-COO- ligands and three nitrogen atoms from one 2-TriPP-COO- ligand with the distorted tricapped trigonal prism geometric configuration. The 2-TriPP-COO- anions acted as the pentadentate ligands and showed two coordination modes which were the pentadentate coordination mode on the backbone and bidentate coordination mode on the arms, respectively. Interestingly, in the bidentate coordination mode, oxygen atoms from the carboxylate group coordinated with the holmium (III) ions by the bidentate chelating coordination mode and the terpyridyl moiety acted as the tridentate-chelating coordination mode was free, these uncoordinated terpyridyl coordination sites were expected to accept palladium(II) ions through post-synthetic modification. Furthermore, the neighboring chains arranged each other through the π•••π stacking and C–H•••π interactions to form a 3D supramolecular structure that was well arranged the uncoordinated terpyridyl sites for coordinating with palladium(II) ions (Fig. 4). The values of the Ho–O and Ho–N bond lengths were in the range of 2.3721(18)-2.467(2)Å and 2.475(2)-2.486(3)Å respectively, they were well agreement with previous studies.[59]

Table 1. Optimization of Heck reaction[a]



Entry	Base	Solvent	T(℃)	Time(h)	Yield(%)[b]
1	K_2CO_3	EtOH	80	1	<10
2	K_2CO_3	H_2O	100	1	<10
3	K_2CO_3	DMF+EtOH	100	1	64.2
4	K_2CO_3	DMF	80	1	84.8
5	Cs_2CO_3	DMF	100	1	92.7
6	KOH	DMF	100	1	88.8
7	**K_2CO_3**	**DMF**	**100**	**1**	**>99**
8	K_2CO_3	DMF	120	1	>99
9	K_2CO_3	DMF	100	6	>99
10[c]	K_2CO_3	DMF	100	1	none
11[d]	K_2CO_3	DMF	100	1	88.6

[a]Reaction conditions: Ph–I (0.5 mmol), methyl acrylate (0.75mmol), base (1.2 mmol), Pd–HoMOF (0.4 mol% Pd). [b]Yield determined by GC-MS analysis. [c]Parent HoMOF as the catalyst. [d]$PdCl_2(CH_3CN)_2$ as the catalyst (0.4 mol% Pd).

Heck coupling reaction. The palladium-catalyzed Heck cross-coupling reaction between aryl halides derivatives and various olefins had been considered one of the most popular methods to

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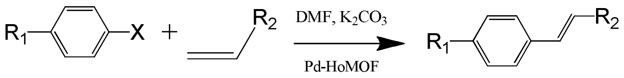
synthesize arylated alkenes in organic chemical reaction. To evaluate the reaction activity of the Pd–HoMOF catalyst, we initially explored the reactions for the palladium catalyzed heck reaction of aryl halides and olefins. The coupling reaction of iodobenzene with methyl acrylate was used as a model reaction to determine the optimum reaction conditions. Through the change of reaction conditions such as reaction time, temperature, solvent and the base, the optimum reaction conditions were confirmed (Table 1), which typically involved an iodobenzene, methyl acrylate and K_2CO_3 in the solution of DMF in the presence of Pd–HoMOF catalyst at 100 °C. Furthermore, it was found that by increasing the amount of Pd–HoMOF catalyst from 0.4 to 1.2 mol% could not improve the yield. Moreover, parent HoMOF exhibited no conversion was observed, this indicated that the catalytic activity of the coupling reaction came from the Pd-HoMOF (entry 10).

Table 2. Results for the Heck reaction catalyzed by Pd–HoMOF[a]



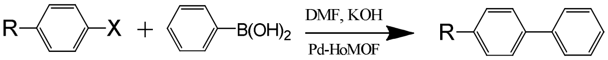
Entry	X	R1	R2	Time(h)	Yield(%)[b]
1	I	H	$COOCH_3$	1	99(>99)
2	I	CH_3	$COOCH_3$	1	95(96.5)
3	I	$COCH_3$	$COOCH_3$	1	99(>99)
4	I	NO_2	$COOCH_3$	1	99(>99)
5	I	H	Ph	1	99(>99)
6	I	CH_3	Ph	1	95(96.7)
7	Br	H	$COOCH_3$	2	99(>99)
8	Br	$COCH_3$	$COOCH_3$	2	96(97.3)
9	Br	CHO	$COOCH_3$	2	96(97.7)
10	Cl	H	$COOCH_3$	6	trace
11	Cl	CH_3	$COOCH_3$	6	trace
12	Cl	CHO	$COOCH_3$	6	17(19.1)

[a]Reaction conditions: aryl halide (0.5 mmol), olefins (0.75 mmol), K_2CO_3 (1.2 mmol), DMF (5 mL), Pd–HoMOF (0.4 mol% Pd), 100 °C. [b]Yield of isolated product after the purification of prep-HPLC (GC-MS yield in parenthesis).

As shown in Table 2, a series of aryl halide derivatives and different olefins had been used as reactants in the Heck cross-coupling to assess the catalytic activity of the Pd–HoMOF. The Heck reaction of iodobenzene with methyl acrylate and styrene both had the high yield (99%; entries 1, 3, 4, 5) in only an hour. When the methyl group presented on the aromatic halide, although it had the negative effect on the yield, it still had the high yield (95%; entries 2 and 6) in only 1 h, which suggested it was the excellent heterogeneous catalyst for the Heck coupling reaction. Furthermore, the coupling of bromobenzene with methyl acrylate also led to an excellent yield (>96%; entries 7-9) in 2 h. However, using the sluggish chlorobenzene as substrate, only little coupling products were obtained even after a reaction time of 6 h (<20%; entries 10-12). That's because the higher bond energy of the C–Cl bond, so it was difficult to activate the aromatic chlorides.

The recyclability of the Pd–HoMOF catalyst (0.4 mol%) was also surveyed by the coupling reaction of iodobenzene with methyl acrylate as a test model. As shown in Table S3, recovery was achieved in five successive reaction runs. To evaluate whether palladium ions were leaching out from the MOF carrier to the solution, we performed the typical hot filtration experiment in the model reaction. The reaction mixture was heated at 100 ℃ for 0.5 h, then the Pd–HoMOF catalyst was removed by hot filtration and the yield for final product was 88%. Only a trace of palladium (ca. 86 ppb) could be detected in the hot filtrate, which was determined by AAS. Although the resulting filtrate was continue heated for another 6 h, no further conversion took place in the filtrate after separation of the Pd–HoMOF catalyst. Since no further conversion was observed, it indicated that Pd–HoMOF was a true heterogeneous catalyst and the soluble species might not be involved in the reactions.

Table 3 Results for the Suzuki–Miyaura coupling reactions catalyzed by Pd–HoMOF[a]



Entry	X	R	Time(h)	Yield(%)[b]
1	I	H	1	99(>99)
2	I	CH_3	1	99 (>99)
3	I	OCH_3	1	99 (>99)
4	I	$COCH_3$	1	99 (>99)
5	I	NO_2	1	99 (>99)
6	Br	H	2	99 (>99)
7	Br	CH_3	2	92(93.5)
8	Br	OCH_3	2	95(96.6)
9	Br	CHO	2	99 (>99)
10	Br	$COCH_3$	2	99 (>99)
11	Cl	H	6	99 (>99)
12	Cl	CH_3	6	92(93.4)
13	Cl	CHO	6	97(98.4)

[a]Reaction conditions: phenylboronic acid (0.75 mmol), aryl halide (0.5 mmol), KOH (1.5 mmol), DMF (5 mL), Pd–HoMOF (0.4 mol% Pd), 100 °C. [b]Yield of isolated product after the purification of prep-HPLC (GC-MS yield in parenthesis).

Suzuki–Miyaura coupling reaction. The Suzuki–Miyaura reaction was also a significant organic reaction for the formation of carbon–carbon bonds in fine chemical synthesis. Encouraged by the interesting results for the Heck reaction, we further evaluated the catalytic activity of the Pd–HoMOF for the Suzuki cross-coupling

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reaction of aryl halide derivatives with phenylboronic acid in the presence of the Pd–HoMOF (0.4 mol%) using KOH as a base in DMF under stirring at 100 °C (Table S4). Our initial exploration of reactions for the palladium catalyzed Suzuki reaction of aryl halides was focused on the coupling of iodobenzene and phenylboronic acid. Within 1 h, a more than 99% isolated yield of the biphenyl was obtained. Other aryl iodides involving electron-donating and electron-withdrawing substituents were also studied and the reaction proceeded with a short time (1 h), with good yield (99%; Table 3). Then we further studied the reaction extending to bromobenzenes and the substituted bromobenzenes that contained electron-donating and electron-withdrawing substituents. With the optimum reaction conditions, it obtained the excellent yields with the corresponding coupling products when different aryl bromide reacted with phenylboronic acid (Table 3, entries 6–10). Furthermore, the coupling of chlorobenzene also provided the target products with excellent yields in the same reaction conditions (Table 3, entries 11–13).

Recyclability of the Pd–HoMOF catalyst (0.4 mol%) was examined in the model reaction of iodobenzene and phenylboronic acid. After completion of the catalytic reaction, the insoluble Pd–HoMOF catalyst could be easily isolated from the reaction mixtures by simple hot filtration alone and could be reused at least five successive reaction runs with not a slight decrease in the reactivity (Table S5). The TEM experiment was carried out on the reused Pd–HoMOF to survey the dispersion morphology of the Pd cations after the catalytic reaction, which were very similar to that before reaction, but there were a few Pd particles aggregation occurred in the Pd–HoMOF while the reaction was progressing (Fig. 2b). This was further confirmed by the similar PXRD patterns after the catalytic reaction (Fig. S6). These experiments indicated that Pd–HoMOF was a true heterogeneous catalyst and the soluble species might not be involved in the reactions.

A probable reaction mechanism by Pd–HoMOF had been proposed (Scheme S1). An oxidative addition of iodobenzene on the exposed Pd(II) center of $[Pd(II)(N)_3Cl]^+$ from the Pd–HoMOF followed by ligand exchange with the phenylboronic acid and KOH were considered as sequential steps. Reductive elimination of biphenyl regenerated the active naked Pd and thereby the hetero-coupling of iodobenzene and phenylboronic acid took place consecutively. Since the active Pd species was generated, no further regeneration step was required and thus the product with a high yield was afforded. [57]

In search of highly active MOF catalysts for Suzuki reactions, a few excellent works deserved particular mention. Suzuki cross-coupling reaction catalyzed by Pd–HoMOF and other various known heterogeneous palladium catalysts were listed in the Table 4. Various solid-supported palladium complexes were studied, they could catalyze the Suzuki coupling reaction under heterogeneous conditions and they could be used several times without loss of the activity.[41-45] Chen et al. studied the Suzuki coupling of chlorobenzene by the molecular Pd(II) complex anchored to UiO-67 in DMF-EtOH at 100℃, which had a high yield (90%), but it required a longer reaction time (20 h).[36] Sen et al. reported the Suzuki coupling reaction of halide benzene with the reusable palladium catalyst synthesized by using the postsynthetic modification method, the super high yield (100%) of substrates derived from iodobenzene was obtained, however, the little product yields (25%) was obtained using chlorobenzene derivatives as substrate.[48] Suzuka et al. reported the Suzuki–Miyaura coupling of bromobenzene by the terpyridine palladium complex anchored to polymer in DMF, which had a lower yield (74%), even heated at 100℃ for 6 hours.[51] Because the grafting of terpyridine palladium complex onto polymer often resulted in random incorporating the active Pd(II) units into the carrier, so they were mutual deactivated between active Pd(II) sites as they were too close to each other.

Table 4 Comparison of the catalytic performances of Pd–HoMOF and other known catalysts in the suzuki–miyaura reactions of phenylboronic acid with aryl halide

Aryl halide	Catalyst	Yield [wt%]	Ref.
Chlorobenzene	Molecular Pd(II) complex anchored to UiO-67	90[a]	36
Chlorobenzene	Pd nanoparticles embedded in MIL-101	97[b]	43
Iodobenzene	Postsynthetic modification of $PdCl_2$ anchored to Sr-MOF-1	100[c]	48
Chlorobenzene	Postsynthetic modification of $PdCl_2$ anchored to Sr-MOF-1	25[d]	48
Bromobenzene	Polymer-supported terpyridine palladium complex	74[e]	51
Iodobenzene	Silica supported terpyridine palladium(II) complex	88[f]	52
Iodobenzene	Pd-containing MOF	97[g]	60
Iodobenzene	Pd–HoMOF	99[h]	This work
Bromobenzene	Pd–HoMOF	99[i]	This work
Chlorobenzene	Pd–HoMOF	99[j]	This work

[a] DMF-EtOH, KOH, 100℃, 20 h; [b] H_2O, NaOMe, 80℃, 20 h; [c] EtOH-H_2O, K_2CO_3, 80℃, 2 h; [d] EtOH-H_2O, K_2CO_3, 80℃, 6 h; [e] H_2O, K_2CO_3, 100℃, 6 h; [f] H_2O, K_2CO_3, 90℃, 1.5 h; [g] Toluene, K_2CO_3, 95℃, 4 h; [h] DMF, KOH, 100℃, 1 h; [i] DMF, KOH, 100℃, 2 h; [j] DMF, KOH, 100℃, 6 h.

Conclusions

In conclusion, the highly dispersed Pd(II) cations had been anchored on the robust HoMOF framework by using the postsynthetic modification coordination incorporation method. The prepared highly efficient single Pd sites heterogeneous catalyst exhibited impressively high activity in Heck and Suzuki cross-coupling reactions for the high-efficiency activation of C–X bond. Furthermore, the catalyst displayed well thermal stability, negligible Pd(II) cations leaching, and could be recovered and reused for five reaction cycles. The successful utilization of strong coordination effect between Pd^{2+} ions and the free polypyridine groups at the skeleton of Ho–MOF could represent a good example in designing highly efficient catalysts for various fine chemical transformations.

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Table of Contents Entry

Postsynthetic modification of single Pd sites into uncoordinated polypyridine groups of a MOF as the highly efficient catalyst for Heck and Suzuki reactions

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A novel Pd-HoMOF catalyst was prepared, which displayed well thermal stability and high activity in Heck and Suzuki cross-coupling reactions.