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Introduction

Homogeneous catalytic systems based on palladium play a very important role in organometallic catalysis, serving as a strategic tool for organic transformation and total synthesis.¹ Because of the limited availability and high price of Pd, from the sustainability point of view it is of great importance to develop Pd catalysts with full utilization of each Pd active site, as well as excellent recyclability and negligible metal leaching in order to reduce the cost of the catalyst and pollution to the environment.² Nevertheless, such a task remains a great challenge to date. Preparation of single-site heterogeneous catalysts represents a suitable solution because single-site heterogeneous catalysts can offer the selectivity and specificity of homogeneous single-site systems combined with easy catalyst separation from reactants and products.³ The immobilization of single-site Pd(π) will not only lead to high activities

A molecular Pd(II) complex incorporated into a MOF as a highly active single-site heterogeneous catalyst for C–Cl bond activation[†]

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The organic palladium complex $Pd(H_2bpydc)Cl_2$ ($H_2bpydc = 2,2'$ -bipyridine-5,5'-dicarboxylic acid) was immobilized on a porous metal-organic framework UiO-67 ($Zr_6O_4(OH)_4(bpdc)_6$, bpdc = *para*-biphenyldicarboxylate) using a direct incorporation strategy. The use of a large amount of the H_2bpdc ligand (90 mol% of the mixed ligands) that can't chelate the Pd complex allowed the formation of isolated Pd single active sites uniformly distributed in the MOF network. Pd(II) doped UiO-67 is isostructural to the parent UiO-67 framework, with a high surface area and pore volume of *ca.* 2000 m² g⁻¹ and 0.79 cm³ g⁻¹, respectively. The material was highly efficient in the catalytic conversion of aryl chlorides, showing remarkably higher activity than the homogeneous Pd counterparts. High yields were achieved in Heck and Suzuki–Miyaura coupling reactions of chloroarenes bearing a wide range of substituents. Moreover, the catalyst was recoverable and reusable, giving essentially identical activity after at least 5 cycles. The combination of the advantages of both homogeneous molecular Pd catalysts and solid MOF structures in this system may bring new opportunity in the development of highly active heterogeneous palladium catalysts for a variety of Pd-catalyzed transformations.

similar to its homogeneous counterparts, but also the advantages of facile separation, possibility of recycling, and potential application to continuous flow processes.⁴ So far, inorganic materials, organic polymers, and membranes have been used as supports to anchor organometallic Pd catalysts.⁵ However, among these systems obtained *via* classical immobilization methods, very few achieve high density as well as uniform distribution of isolated active single-sites. For example, the grafting of molecular Pd catalysts onto organic polymers often results in random anchoring of the ligands or active units on the support, and consequently, mutual deactivation between sites that are too close to each other, and significantly reduced efficiency compared to their homogenous counterparts.^{6,7} Therefore, it is essential to develop a heterogeneous Pd(II) catalytic system with a high Pd density as well as isolated single active sites.

Metal–organic frameworks (MOFs) have emerged as an important class of functional materials owing to their high surface area, porosity, and chemical tunability.⁸ In recent years, the employment of MOFs as heterogeneous catalysts has attracted tremendous interest, especially in the use of MOFs as scaffolds for the encapsulation of metal (*e.g.*, Pd, Au, Ru, and Pt) nanoparticles.⁹ However, little attention has been paid to the immobilization of metal ions on MOFs as single-site catalysts.¹⁰ With open and uniform channel structures, MOFs are particularly suitable for immobilizing well-defined molecular catalysts with a high degree of metal dispersion. Recent reports have illustrated some examples where palladium ions



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Paper

are anchored on MOFs through direct or post-synthesis incorporation. Post-synthesis modification has been applied to generate Pd(II)@MOFs,¹¹ but the metal salts used as precursors tend to aggregate on the surface, leading to serious pore blocking and a random distribution of Pd active sites on the MOF.⁶ While direct incorporation of organometallic catalysts into the framework of MOFs allows completely isolated and uniform catalytic centers to form, it has not been extensively investigated.⁷ A literature survey shows that there are only few examples reporting the synthesis of Pd(II)@MOFs as heterogeneous catalysts using the direct incorporation method.^{12,13} These Pd(II)@MOF catalysts were mostly utilized for carboncarbon (C-C) coupling reactions. While this reaction represents one of the most useful transformations in organic synthesis, the reported studies were shown to be efficient only for the activation of aryl bromides and iodides in the couplings.¹³ From a practical point of view, the use of aryl chlorides is desirable because they are arguably the most useful class of aryl halide substrate, due to their lower cost and the wider diversity of available compounds. However, the activation of aryl chlorides is much more difficult than aryl bromides or iodides. The inefficiency of these Pd(II) containing MOFs in the activation of aryl chlorides could be attributed to their low specific surface area (BET, less than 100 m² g⁻¹) after Pd modification or the small distance between the loaded Pd cations (Pd...Pd = 3-4 Å, too short to attain single-site catalyst activity).¹⁴

Herein, we report the coupling reactions of aryl chlorides over a palladium(II) complex, H_2L_1 (Pd(H_2 bpydc)Cl₂, H_2 bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid), which was built in a robust MOF using a direct incorporation method (Scheme 1). We have chosen the UiO-67 type MOF for the incorporation of the Pd complex because the UiO family of MOFs based on $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units (SBUs) and dicarboxylate bridging ligands possesses high specific surface areas with unprecedented stability.¹⁵ In contrast to the previous reports on the synthesis of Pd(II)@MOFs by direct incorporation methods, in this work we have successfully developed a novel mixed ligand strategy to prepare the MOF host in order to obtain isolated Pd single active sites in the MOF network in a uniform way for highly efficient catalysis reactions. The use of a large number of the H₂L₂ (H₂bpdc, bpdc = *para*-biphenyl-



Scheme 1 Schematic representation of the synthesis of Pd(II) doped UiO-67. The structure model (right) of Pd(II) doped UiO-67 shows the incorporation of the L₁ ligand into the framework. Colour coding: zirconium, purple; carbon, grey; oxygen, red; nitrogen, blue; palladium, yellow; chlorine, green. All H atoms are omitted for clarity.

dicarboxylic acid) ligands (90 mol% of the mixed ligands) that can't chelate the Pd complex is essential in reducing the Pd usage as well as in ensuring the separation and dispersion of the metalloligand H_2L_1 and the single Pd cations in the individual cages of the MOF architecture, and thus preventing the Pd catalysts from mutual deactivation between sites that are too close together. It can be anticipated that such a rational design will lead to the highest single-site catalyst activity compared with the other reported Pd(II)@MOFs because it allows maximum exposure of the active sites to reactants. The prepared palladium catalyst shows high activity in the Heck and Suzuki-Miyaura coupling reactions of a variety of aryl chlorides. Moreover, the catalyst was recoverable and reusable, giving essentially identical activity after at least 5 cycles. Metal leaching was largely inhibited because of the strong interaction between Pd(II) and the MOF network. This protocol coincides with the concept of green chemistry as it could reduce the cost of catalysis and additional purification of the final product as well as the potential heavy-metal pollution to the environment. To the best of our knowledge, this work represents the first example of the incorporation of a palladium complex into MOFs for the efficient activation of aryl chlorides for carbon-carbon coupling reactions.

Experimental section

Materials preparation

Synthesis of (2,2'-bipyridine)-5,5'-dicarboxylic acid dimethyl ester (Me₂bpydc). An appropriate amount of (2,2'-bipyridine)-5,5'-dicarboxylic acid (500 mg, 2 mmol) in methanol (30 mL) was added to concentrated sulfuric acid (2 mL), which had been placed in an ice bath. After refluxing overnight, the solution was poured into water (40 mL), forming a white slurry. The pH of the slurry was adjusted to 7 with powdered Na₂CO₃. The product was then extracted with chloroform, dried over magnesium sulfate and evaporated to dryness. ¹H NMR (400 MHz, CDCl₃) δ = 9.24 (s, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H).

Synthesis of [(5,5'-dimethoxylcarboxyl-2,2'-bipyridine-)palladium(\mathfrak{n})]dichloride (Me₂L₁). A mixture of PdCl₂(CH₃CN)₂ (130 mg, 0.5 mmol) and dimethyl (2,2'-bipyridine)-5,5'dibenzoate (Me₂bpydc) (136 mg, 0.5 mmol) in 8 mL of CH₃CN was stirred at 65 °C for 24 hours. The resulting yellow solid was collected by filtration and was washed with CH₃CN, and then was heated at 100 °C for 12 h under vacuum.

Synthesis of [(5,5'-dicarboxy-2,2'-bipyridine-)palladium(π)]dichloride (H₂L₁). A solution of [(5,5'-dimethoxylcarboxyl-2,2'bipyridine-)palladium(π)]dichloride (Me₂L₁) (120 mg, 0.27 mmol) in tetrahydrofuran (THF) (10 mL), ethanol (10 mL), and 3 M aqueous NaOH (10 mL) was stirred at 70 °C for 5 hours. The solution was cooled to room temperature and acidified to pH 1. A yellow solid was obtained, and washed with H₂O and methanol to afford the product. ¹H NMR (400 MHz, D₂O) δ = 8.79 (s, 2H), 8.61 (d, *J* = 8.4 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 2H). Published on 03 July 2014. Downloaded by UNIVERSITY OF BRIGHTON on 17/07/2014 13:25:24.

Synthesis of Pd(π) doped UiO-67. ZrCl₄ (70.0 mg, 0.3 mmol), H₂L₁ (12.6 mg, 0.03 mmol) and H₂L₂ (H₂bpdc, *para*-biphenyldicarboxylic acid) (65.4 mg, 0.27 mmol) were dispersed in DMF (10 mL) and sealed in a 25 mL tube at 100 °C for 36 hours. The produced powders were isolated by centrifugation and dried at ambient temperature. Subsequently, the as-synthesized sample was soaked in chloroform for three 18 hours periods at room temperature to remove DMF and ligand precursors, then filtered off and dried under vacuum at room temperature for 24 h. Finally, the sample was heated under vacuum at 150 °C overnight to remove the solvents.

Catalyst characterization

The BET surface area measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before the analysis, the samples were evacuated at 150 °C for 12 h.

Powder X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu K α radiation (40 kV, 30 mA, λ = 0.1543 nm). The size and morphology of the Pd(π) doped UiO-67 were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010HR) with EDX analysis (Oxford INCA EDS) operated at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10⁻⁹ Torr. The palladium content of the samples were determined quantitatively by AAS on a HITACHI Z-2300 instrument.

Catalytic experiments

Heck coupling reaction. Typically, aryl halide (0.5 mmol), olefin (0.75 mmol), K₂CO₃ (1.5 mmol), TBAB (0.3 mmol), hexamethylbenzene (0.3 mmol, as an internal standard for GC analysis), and palladium catalyst (0.46 mol%) were added to 5 mL DMF. The reaction mixture was stirred at the desired temperature under a N₂ atmosphere. The solution was filtered and washed with brine and diethyl ether. The organic phase was subsequently extracted with diethyl ether $(3 \times 20 \text{ mL})$, dried over MgSO₄, and concentrated in vacuo. The crude product was quantified by GC-MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column). The product was purified by silica gel chromatography. The product identification was conducted by GC-MS analysis and ¹H NMR and ¹³C NMR measurement on a Bruker Advance 600 spectrometer or a Bruker DRX-400 spectrometer using CDCl₃ as a solvent and TMS as an internal standard.

Suzuki–Miyaura coupling reaction. Typically, aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), KOH (1.5 mmol), hexamethylbenzene (0.3 mmol, as an internal standard for GC analysis), and palladium catalyst (0.46 mol%) were added to a DMF–EtOH mixture (5 mL DMF and 0.25 mL EtOH). The reaction mixture was stirred at the desired temperature under a N_2 atmosphere. The solution was filtered and washed with brine and diethyl ether. The organic phase was subsequently extracted with diethyl ether (3 × 20 mL), dried over MgSO₄, and concentrated *in vacuo*. The crude product was quantified by

GC-MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm \times 30 m DB-WAX capillary column). The product was purified by silica gel chromatography. The product identification was conducted by GC-MS analysis and ¹H NMR and ¹³C NMR measurement on a Bruker Advance 600 spectrometer or a Bruker DRX-400 spectrometer using CDCl₃ as a solvent and TMS as an internal standard.

The recyclability tests

The reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the catalyst was isolated from the reaction solution at the end of the reaction, washed with DMF, and then heated at 150 $^{\circ}$ C under vacuum.

Results and discussion

The [PdCl₂(bpy)]-derived dicarboxylic acid H₂L₁ was synthesized by treating PdCl₂(CH₃CN)₂ with dimethyl (2,2'-bipyridine)-5,5'-dicarboxylate, followed by base-catalyzed hydrolysis. A mixture of H_2L_1 and H_2L_2 with a molar ratio of 1:9 was then prepare Pd(II) doped UiO-67 with used to the $Zr_6O_4(OH)_4(L_1)_x(L_2)_{6-x}$ formula, which allowed the incorporation of the H₂L₁ ligand into the UiO-67 framework with biphenyldicarboxylate (bpdc) as the bridging ligand. Powder X-ray diffraction (XRD) patterns of the Pd(II) doped UiO-67 were identical to those of the parent UiO-67 (Fig. 1), indicating that Pd(II)-UiO-67 is isostructural to the parent UiO-67. In order to confirm that L1 was really embedded into the network of the MOF as proposed in Scheme 1, we have performed an elemental analysis on the Pd doped UiO-67 sample which indicated the N content was ca. 0.31 wt%. Based on the elemental analysis results, the molar ratio of $L_1/(L_1 + L_2)$ was calculated to be ca. 4.0%, giving a theoretical Pd content of ca. 1.16 wt% with the assumption that all 2,2-bipyridine moieties were bonded with PdCl₂. This value was very close to the actual Pd quantity (1.1 wt%) in the Pd doped UiO-67 as measured by AAS. From the structure model depicted in Scheme 1 (and



Fig. 1 Powder XRD patterns of UiO-67 (a), and Pd(II) doped UiO-67 samples recorded before (b) and after (c) the catalytic reactions.

Fig. S1[†]), the molar ratio of $L_1/(L_1 + L_2)$ of the displayed structure was calculated to be *ca*. 4.17 mol%, which is in good agreement with the actual value measured in the MOF material. These results are consistent with the structure model of the prepared Pd doped UiO-67 material shown in Scheme 1.

The surface area and pore volume of the Pd-MOF were determined from N_2 adsorption/desorption isotherms at 77 K (Fig. 2), and were calculated to be *ca.* 2000 m² g⁻¹ and 0.79 cm³ g⁻¹, respectively. The mean pore size obtained from the Horvath–Kawazoe model was *ca.* 7.0 Å. The high porosity of the framework allows close contact between the reactants and the Pd catalytic centers, and facilitates substrate diffusion for efficient catalysis.

To evaluate the level of possible aggregation of the Pd cations during the MOF synthesis, TEM experiments were carried out on the Pd(u) doped UiO-67 material. The results shown in Fig. 3 suggest that there were no distinctly congregated Pd particles in the MOF. To confirm that the Pd ions were coordinated to 2,2'-bipyridine (bpy) moieties prior to the



Fig. 2 Nitrogen adsorption (♦)/desorption (◊) isotherms at 77 K (top) and micropore size distribution (bottom) of 1.1 wt% Pd(II) doped UiO-67.



Fig. 3 TEM images of Pd(II) doped UiO-67 (a and b).

doping reactions, and to determine their coordination environment within the framework, we performed X-ray photoelectron spectroscopy (XPS) analysis on PdCl₂(CH₃CN)₂, Me₂L₁ (dimethyl esters of L_1), and Pd(II)–UiO-67 samples. Fig. 4(a) shows that both Me_2L_1 and Pd(II) doped UiO-67 samples exhibit a Pd 3d_{5/2} band at around 338 eV, which is characteristic of divalent Pd. For comparison, the XPS spectrum of pristine PdCl₂(CH₃CN)₂ was also measured which confirmed the Pd(II) environment. However, the Pd 3d lines of PdCl₂(CH₃CN)₂ appear shifted to a higher binding energy compared to the Pd 3d line of the other two compounds. This can be interpreted as a similar Pd environment in both the MeL₁ and Pd(π) doped UiO-67 compounds, where the neighboring N is not involved in a C≡N bond, but rather, placed in a C-N-C delocalized environment. This is confirmed by the N 1s spectra shown in Fig. 4(b), which indicate a larger binding energy for the N 1s peak of the reference $PdCl_2(CH_3CN)_2$ with respect to those of the other two species. The absence of multiple features in the N 1s spectrum of the Pd(II) doped UiO-67 seems to further confirm the presence of only one environment for N, namely each Pd is bonded to the uncoordinated 2,2'-bipyridine units. Additionally, the EDX analysis shows that the atomic ratio of Pd : Cl is ca. 1 : 2 (Fig. S2[†]), which confirms that all the palladium remains in its dichloride form.

The palladium-catalyzed Heck coupling reaction is well known as a powerful and versatile method to synthesize arylated alkenes in fine chemical synthesis. Our initial studies focused on the Heck reaction of aryl chlorides with olefins to evaluate the catalytic activity of the Pd(II) doped UiO-67 material. First, we chose 4-chloroacetophenone as substrate to screen the reaction parameters. The reactions were carried out with Pd(II) doped UiO-67 as a catalyst and DMF as a solvent under a N₂ atmosphere, and different bases were used (Table 1, entries 1–4). It was found that potassium carbonate worked the best compared with KOH, Cs_2CO_3 and K_3PO_4 , while the yield of the coupling product was still very low. An



Fig. 4 XPS spectra of Pd(II) doped UiO-67, Me₂L₁, and PdCl₂(CH₃CN)₂ referenced to hydrocarbon C 1s. (a) Pd 3d; (b) N 1s; and (c) survey photoemission spectrum of Pd(II) doped UiO-67. The inset in (c) indicates the Pd 3d and Zr 3p peak positions.

Table 1 Heck coupling of 4-chloroacetophenone with $\mathsf{Pd}({\scriptstyle II})$ doped UiO-67ª

O CI + CI + CI + Catalyst Dase, solvent O Ja								
Entry	Base	Solvent	Т (°С)	Additive	Time (h)	Yield ^b (%)		
1	КОН	DMF	100	_	20	5		
2	K_2CO_3	DMF	100	_	20	15		
3	Cs_2CO_3	DMF	100	_	20	11		
4	K_3PO_4	DMF	100		20	7		
5	K_2CO_3	DMF	120		20	18		
6	K_2CO_3	DMF	100	TBAB	20	95		
7	K_2CO_3	Ethylene glycol	100	TBAB	24	8		
8 ^c	K_2CO_3	DMF + EtOH	100	TBAB	24	50		
9	K_2CO_3	H_2O	100	TBAB	24	5		
10	K ₂ CO ₃	DMF	100	TBAB	24	99		
11^d	K_2CO_3	DMF	100	TBAB	24	_		
12^e	K_2CO_3	DMF	100	TBAB	24	49		
13^f	K_2CO_3	DMF	100	TBAB	24	34		
14^g	K_2CO_3	DMF	100	TBAB	24	_		
15 ^{<i>h</i>}	K ₂ CO ₃	DMF	100	TBAB	24	—		

^{*a*} Reaction conditions: 4-chloroacetophenone (0.5 mmol), phenylethylene (0.75 mmol), base (1.5 mmol), solvent (5 mL), Pd(II) doped UiO-67 (0.46 mol% Pd), TBAB (0.3 mmol), under N₂. ^{*b*} Yields were determined by GC-MS analysis. ^{*c*} DMF (5 mL) and EtOH (0.25 mL). ^{*d*} Parent UiO-67 as the catalyst. ^{*e*} Me₂L₁ as the catalyst. ^{*f*} PdCl₂(CH₃CN)₂ as the catalyst (0.46 mol% Pd). ^{*g*} PdCl₂(CH₃CN)₂ as the catalyst (46 ppb Pd). ^{*h*} PdCl₂ as the catalyst (46 ppb Pd).

increase of temperature from 100 to 120 °C didn't promote the reaction significantly (entry 5). The addition of tetrabutyl-ammonium bromide (TBAB) enhanced the yield remarkably (entry 6), presumably due to the stabilization effect of TBAB for the palladium species.¹⁶ The influence of solvent on the catalytic performance of the present reaction system was investigated with the optimized base. It was reported that alcohol can act as a hydrogen bond donor, and thus promote the dissociation of halides and facilitate the reaction.¹⁷ However, in the present work we found that the use of ethylene glycol, ethanol mixed with DMF, or H₂O as solvent were all ineffective for this transformation (entries 7–9). A maximum of 99% conversion of 4-chloroacetophenone (**1a**) was achieved with >99% selectivity to 4-aceto-1,1'-biphenyl (**3a**) in 24 hours (entry 10).

Parent UiO-67 showed no signs of conversion, confirming that the catalytic activity came from the Pd doped ligand (entry 11). For comparison, the reactivity of Me_2L_1 , *i.e.* the esterified L_1 ligand of the MOF, in the Heck reaction was also examined under identical conditions. As shown in Table 1, the yield of the desired coupling product was very low when using Me_2L_1 as the catalyst (Table 1, entry 12). Therefore, we believe that the incorporation of the metalloligand H_2L_1 into the porous frameworks could stabilize the Pd catalytic center by efficiently isolating the sites in a manner similar to the peptide architecture of enzymes in biological systems. To further confirm that the Pd atoms were successfully grafted on the bpy moieties of the MOF rather than simply adsorbed on the solid surface, PdCl₂(CH₃CN)₂ was employed as a catalyst for the same reaction (entry 13). The poor yield of the coupling product demonstrated that Pd was immobilized on the bpy moieties in the Pd(π) doped UiO-67. It is well known that Pd(π) ions are easily aggregated under such conditions, losing their catalytic activity gradually. However, in the case of Pd(π) doped UiO-67, the 2,2'bipyridine moieties in the MOF could provide a strong coordination environment for the immobilization of palladium, thus preventing the agglomeration of Pd species during the reaction.

Different aryl chlorides were employed in the reaction (Table 2) to investigate the range of aryl chlorides that can be tolerated in the Heck coupling reaction. Aryl chlorides of various electronic characters reacted smoothly with styrene (Table 2, entries 1–7). In general, electron-deficient aryl chlorides exhibit higher activity than electron-rich ones. Heteroaryl chlorides, *e.g.* 2-chloropyridine, also underwent coupling smoothly and furnished the desired products in excellent yields (entry 7).

We further investigated the coupling of different alkenes with 4-chloroacetophenone. As shown in Table 2, styrene derivatives reacted nicely with 4-chlorobenzaldehyde. For example, 4-methylstyrene and 4-fluorostyrene afforded the corresponding coupling products in 96% and 94% yield, respectively (Table 2, entries 8 and 9). Also, the reactions of methyl- or ethyl-acrylate with 4-chloroacetophenone both gave the desired products in excellent yields (entries 10 and 11). In particular, alkyl-substituted terminal olefins (*e.g.* octene), which usually have low reactivity in the documented Heck reactions, were found to be coupled in good yields (entry 12).

The catalytic efficiency of Pd doped UiO-67 is superior to that of the less porous catalysts with a similar building unit. For example, the reaction of chlorobenzene and styrene in the presence of Pd(π) doped UiO-67 produced the *trans*-1,2-diphenylethylene product in 81% yield (Table 2, entry 5), while the catalyst (Ln₂[Pd(bpydc)Cl₂]₂[Pd(Hbpydc)Cl₂]₂, Ln = Sm, Eu, Gd, or Tb) reported in the literature gave essentially no coupling product (<5% yield) under similar conditions.^{13*a*} The low activity of the latter which has a similar building unit to that prepared in this study may be attributed to the framework structure, which has low porosity and small distances between Pd…Pd (only 3.3–3.70 Å) that would restrain their catalytic activity significantly.

The Pd(π) doped UiO-67 could be easily recovered by centrifugation after removing the supernatant and washing with DMF several times. The recovered catalyst was subsequently used in successive runs without any loss of catalytic efficiency (Table 2, entry 13). PXRD patterns for the used catalyst suggest that the structural integrity of the MOF material was mostly maintained after the catalytic reactions (Fig. 1). XPS measurements of the recovered solid confirmed that the palladium remained in its divalent form after the reaction (Fig. S3†). The heterogeneous nature of Pd(π) doped UiO-67 was investigated by a hot filtration experiment. The reaction in the presence of Pd(π) doped UiO-67 was allowed to proceed only to approximately 28% conversion. At this point, the solution was quickly filtrated and the solid was removed. The filtration was per-

Table 2 Heck coupling reactions of various aryl chlorides with olefins over Pd(II) doped UiO-67^a

	R1	L CI + R base, solvent R	3	
Entry	Aryl chloride	Olefin	Product	$\operatorname{Yield}^{b}(\%)$
1	° cila	└──── 2a	°,−,⊂,⊂,⊂,⊂,,,,,,,,,,,,,,,,,,,,,,,,,,,,	96
2	o ₂ N-C ^I 1b	└─── 2a	o _z n-	97
3	F ₃ C-Cl ₁ c	└─── 2a	F ₅ C	95
4	NC-CI1d	└─── 2a	NC 3d	96
5		└──── 2a		81
6		└──── 2a		95
7 ^{<i>c</i>}		≌2a		90
8	S-c-Ia	∑F_2b	°→⊂∽→ [−] 3h	96
9	° cila	└─── 2c	°	94
10	° cila	⇒Ů₀~2d	۶-۲- ⁻ -3i	97
11		~~2f	}∽, , , , , , , , , , , , , , , , , , ,	90
12		≫ ⁴⁵ 2g		85
13 ^{<i>d</i>}		∑_2a	°→⊂⊂⊂3a	95

Catalyst

^{*a*} Reaction conditions: aryl chloride (0.5 mmol), phenylethylene (0.75 mmol), K_2CO_3 (1.5 mmol), DMF (5 mL), Pd(1) doped UiO-67 (0.46 mol% Pd), TBAB (0.3 mmol), 100 °C, 24 h, under N_2 . ^{*b*} Isolated yield based on 1. ^{*c*} 0.7 mol% Pd, 120 °C. ^{*d*} The fifth cycle.

formed at the reaction temperature in order to avoid re-deposition of dissolved palladium upon cooling. Only a trace of palladium (ca. 46 ppb) could be detected in the hot filtrate. The isolated solution was allowed to further react for 20 h, however, no further reactivity was observed under similar reaction conditions (Fig. S4[†]). Moreover, a very small amount of dissolved palladium (less than 0.1% of the total palladium) was detected in the solution at the end of the reaction. In order to assess the possible contribution of the leached Pd to the catalytic activity of Pd(II) doped UiO-67, we performed the reaction using the same amount of dissolved palladium (ca. 46 ppb) under the same reaction conditions. No appreciable conversions of 4-chloroacetophenone were observed (Table 1, entries 14 and 15). Although it cannot be excluded that such a low amount of palladium in solution may be active for the reaction, it could be concluded that this contribution to the overall activity for the Pd(II) doped UiO-67 is very limited and

the reaction is predominantly heterogeneous. The Pd content of the reused catalyst was almost the same as the fresh one, as determined by AAS. These studies indicated that the loss of palladium active sites was negligible, which could account for the preservation of the catalytic activity of this catalytic system.

Encouraged by these interesting results, we further examined the catalytic activity of the Pd(II) doped UiO-67 for the Suzuki-Miyaura coupling reaction of aryl chlorides with phenylboronic acid. The reaction parameters were first screened using 4-nitro-1-chlorobenzene as a substrate (Table S1[†]). The best result was obtained when a DMF-EtOH mixture was used as a solvent and K₂CO₃ was used as a base, which afforded the desired product in 97% isolated yield (Table 3, entry 2). Under the optimized conditions, different aryl chlorides reacted smoothly with phenylboronic acid to give the corresponding cross-coupling products in good to excellent yields (Table 3, entries 1-10). In general, aryl chlorides substituted with elec-

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Table 3 Suzuki–Miyaura coupling reactions of various aryl chlorides over Pd(μ) doped UiO-67^a



^{*a*} Reaction conditions: aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol), KOH (1.5 mmol), DMF (5 mL), EtOH (0.25 mL), and Pd(II) doped UiO-67 (0.46 mol% Pd), 100 °C, 20 h, under N_2 . ^{*b*} Isolated yield based on 1. ^{*c*} 0.7 mol% Pd, 120 °C.

tron-withdrawing groups (e.g., 4-CN, 4-COMe, 4-NO₂, and 4-CF₃) exhibited higher activity than electron-rich ones (entries 1-7). Notably, even 2-chloroanisole (1i), which is both deactivated and sterically hindered, also worked well and gave the corresponding coupling product in 80% yield (entry 8). Moreover, heteroaryl chlorides could also be coupled giving excellent yields (entries 9 and 10). These results demonstrate the general applicability of this novel catalytic system for Suzuki-Miyaura coupling reactions. The much lower activities observed for the parent UiO-67 and $\mathrm{Me_{2}L_{1}}$ as well as Pd complexes (Table S1[†]) further confirms the importance of highly dispersed single-site Pd(II) immobilized on MOFs in achieving activity for various carbon-carbon coupling а high transformations.

Conclusions

In conclusion, we have successfully immobilized highly dispersed Pd(n) cations on the robust UiO-67 framework by using a direct incorporation method. The prepared material acted as a highly active single-site heterogeneous catalyst for the efficient activation of C–Cl bond in the Heck and Suzuki-Miyaura coupling reactions of aryl chlorides bearing a variety of substituents. In addition, the catalyst was easily recoverable and reusable. Such a rational design for single-site catalysts with full utilization of each Pd active site, as well as excellent recyclability and negligible metal leaching could coincide with the concepts of green chemistry. This success in the preparation of single-site heterogeneous Pd catalysts by simply immobilizing organometallic palladium onto MOFs might bring new opportunities in the development of highly active heterogeneous palladium catalysts for C–C couplings or other Pd-catalyzed transformations.

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Notes and references

- (a) A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973; (b) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4442.
- 2 M. Flytzani-Stephanopoulos and B. C. Gates, *Annu. Rev. Chem. Biomol. Eng.*, 2012, **3**, 545.
- 3 (a) J. M. Thomas, R. Raja and D. W. Lewis, Angew. Chem., Int. Ed., 2005, 44, 6456; (b) D. T. Genna, A. G. Wong-Foy,
 A. J. Matzger and M. S. Sanford, J. Am. Chem. Soc., 2013, 135, 10586.
- 4 (a) J. A. Gladysz, Chem. Rev., 2002, **102**, 3215; (b) L. X. Dai, Angew. Chem., Int. Ed., 2004, **43**, 5726.
- 5 C. Copéret, M. Chabanas, R. P. Saint-Arroman and J. M. Basset, *Angew. Chem., Int. Ed.*, 2003, **42**, 156.
- 6 J. Canivet, S. Aguado, Y. Schuurman and D. Farrusseng, J. Am. Chem. Soc., 2013, 135, 4195.
- 7 F. Song, C. Wang, J. M. Falkowski, L. Ma and W. B. Lin, J. Am. Chem. Soc., 2010, 132, 15390.
- 8 (a) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, 38, 1213; (b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, 112, 724.
- 9 (a) B. Yuan, Y. Pan, Y. W. Li, B. Yin and H. Jiang, Angew. Chem., Int. Ed., 2010, 49, 4054; (b) H. Liu, Y. Liu, Y. W. Li, Z. Tang and H. Jiang, J. Phys. Chem. C, 2010, 114, 13362; (c) F. Schröder, D. Esken, M. Cokoja, M. W. E. van den Berg, O. I. Lebedev, G. van Tendeloo, B. Walaszek, G. Buntkowsky, H. H. Limbach, B. Chaudret and R. A. Fischer, J. Am. Chem. Soc., 2008, 130, 6119; (d) A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Ronnebro, T. Autrey, H. Shioyama and Q. Xu, J. Am. Chem. Soc., 2012, 134, 13926.
- 10 (a) C. Wang, Z. Xie, K. E. deKrafft and W. B. Lin, J. Am. Chem. Soc., 2011, 133, 13445; (b) O. K. Farha, A. M. Shultz,

A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem.* Soc., 2011, **133**, 5652; (c) D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. W. Wei and H. C. Zhou, *Angew. Chem., Int.* Ed., 2012, **51**, 10307.

- 11 (a) D. J. Lun, G. I. N. Waterhouse and S. G. Telfer, J. Am. Chem. Soc., 2011, 133, 5806; (b) G. Q. Kong, S. Ou, C. Zou and C. Wu, J. Am. Chem. Soc., 2012, 134, 19851;
 (c) C. J. Doonan, W. Morris, H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 9492;
 (d) S. Hossain, M. J. Jin, J. Park, Y. Qian and D. A. Yang, Catal. Lett., 2013, 143, 122.
- 12 A. D. Burrows, M. F. Mahon and C. T. F. Wong, *CrystEng-Comm*, 2008, **10**, 487.
- 13 (a) S. L. Huang, A. Q. Jia and G. X. Jin, *Chem. Commun.*, 2013, **49**, 2403; (b) S. Zhang, Q. Liu, M. Shen, B. Hu,

Q. Chen, H. Li and J. P. Amoureux, *Dalton Trans.*, 2012, **41**, 4692; (c) T. Osako and Y. Uozumi, *Heterocycles*, 2010, **80**, 505; (d) Y. M. A. Yamada, Y. Maeda and Y. Uozumi, *Org. Lett.*, 2006, **8**, 4259.

- 14 J. Hafizović, A. Krivokapic, K. C. Szeto, S. Jakobsen, K. P. Lillerud, U. Olsbye and M. Tilset, *Cryst. Growth Des.*, 2007, 7, 2302.
- 15 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, 130, 13850.
- 16 (a) M. R. Buchmeiser and K. Wurst, J. Am. Chem. Soc., 1999,
 121, 11101; (b) V. Caló, A. Nacci, A. Monopoli, S. Laera and N. Cioffi, J. Org. Chem., 2003, 68, 2929.
- 17 J. Ruan, J. A. Iggo, N. G. Berry and J. L. Xiao, *J. Am. Chem. Soc.*, 2010, **132**, 16689.