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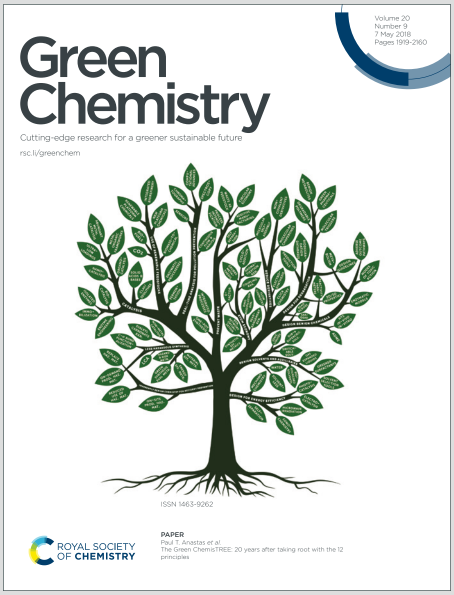

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DOI: 10.1039/C9GC01993F

ARTICLE

An *N*-Heterocyclic Carbene Functionalised Covalent Organic Framework: Atomically Dispersed Palladium Catalyst for Coupling Reactions under Mild Condition

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Covalent organic frameworks (COFs) are a new class of crystalline porous materials that could function as excellent scaffold in heterogeneous catalysts. Herein, we report a functionalised COF (COF-NHC) using *N*-heterocyclic carbene (NHC) as a monomer building block via a facile ionothermal strategy. The simple and easily prepared imine-linked COF-NHC possessed two coordination sites (NHC and amine), which could fix the active component (Pd) tightly in COF, leading to atomically dispersed Pd in a heterogeneous catalyst. The as-prepared Pd@COF-NHC showed high stability in Suzuki-Miyaura coupling reaction of arylboronic acid and aryl halides in aqueous media at room temperature, and could be easily recycled and reused multiple times without loss of catalytic activity. Meanwhile, C-C coupling reaction could be accomplished using triarylbismuth reagents in ethanol aqueous solution for high yields.

Introduction

Construction of the carbon-carbon (C-C) bond has become an extremely powerful tool in natural product synthesis, medicinal chemistry, materials science, catalysis, and coordination chemistry [1]. A large number of strategies for the C-C cross-coupling reaction have been developed, including the nickel, gold and palladium complexes. The application of palladium as catalyst has attracted increasing attention for the high activity [2]. Recently, a few heterogeneous catalytic systems were developed by immobilising palladium-NHC (NHC = *N*-heterocyclic carbene) on various supports such as silica, zeolite, SBA and MCM: displaying improved environmental friendliness, stability and reusability. Nevertheless, these reported approaches suffer from drawbacks such as requiring relative long reaction times and high reaction temperatures. Therefore, more efficient and recyclable new catalyst systems are needed for the C-C coupling reaction.

Covalent organic frameworks (COFs) are of great practical interest in recent years owing to their low atomic-weight elements and tunability of composition/structure/function, with many potential applications in e.g. gas adsorption, energy storage, sensing and especially in heterogeneous catalysis [3]. Heterogeneous catalysts in synthetic chemistry can be efficiently separated and recycled [4], and the COF are considered ideal candidates in this area for their excellent properties with crystallinity, tunable channels, and high stability [5]. Wang and co-workers reported several crystalline COFs with catalytic applications in Suzuki coupling reaction [6] and asymmetric aldol reaction [7]. Zhang *et al.* reported a thioether-containing COF that could be applied to nitrophenol reduction and Suzuki-Miyaura coupling reaction [8]. However, although all these catalysts showed good stability and recyclability, their use still required relatively high temperature and/or long reaction time, due to a lack of efficient functional ligand to support the metal catalyst in COFs. Therefore, choosin a highly efficient functional catalytic ligand could be viewed as an effective route to explore the construction of COFs and their use in organic synthesis.

NHCs are a class of functional ligands desirable in COFs [9] due to their many inherent advantages, such as strong σ-donating ability, thermal and oxidative stability, as well as green application in aqueous solution. NHCs-supported Pd complexes have been extensively studied in organometallic chemistry as catalysts in the C-C cross-coupling reaction [10]. Recently, we have reported a series of homogeneous NHCs/$PdCl_2$ that exhibit high catalytic activity and environmental friendliness at room temperature [11]. Still, developing highly active NHC-containing heterogeneous catalysts with recyclability and reusability remains a challenge [4a,12]. Now two imidazolium-based COFs were reported and used as CO_2 adsorbents [9a, 13], the NHC functionalised COFs will be widely applicated to the material and catalyst areas.

In this work, an NHC functionasized, palladium(II)-coordinated COF material (denoted as Pd@COF-NHC, Scheme 1) was designed, synthesised, and applied in catalysing the C-C

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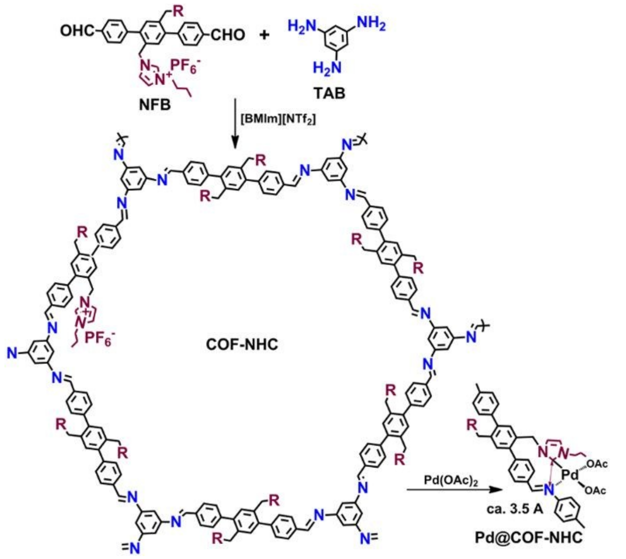
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1 Schematic representation of COF-NHC and Pd@COF-NHC synthesis.

coupling reaction for the first time. The distance from the nitrogen atom of imine and adjacent carbene carbon of NHC is ~ 3.5 Å, making it an ideal chelating ligand for incorporating Pd ions. In this way, the mononuclear metal ions will be highly dispersed and fixed firmly in the frameworks [8a]. The designed Pd@COF-NHC should have three features: (i) heterogeneous catalyst that could be easily separated; (ii) highstability in water, alkali solutions, and most organic solvents; (iii) high activity and reusability.

Results and discussion

Catalyst preparation and characterisation

Design of catalyst. The preparation of the heterogeneous catalyst Pd@COF-NHC involved two steps: direct construction of the COF-NHC covalent organic framework, and post-modification of Pd active component (Scheme 1).

Synthesis of COF-NHC. As shown in Scheme 1, the imine-linked 2D COF-NHC material was synthesised by the condensation reaction of triangular building blocks of 1,3,5-triaminobenzene (TAB) and the bi-NHC substituted 1,4-di(4-formylbenzyl)-benzene (NFB). The linear block of NFB, an ionic compound, was synthesised by six steps (see SI for details). Care should be taken during the design of the COFs to simultaneously satisfy the functionality and crystallinity requirements. Considering the imidazole group of monomers and the structure-directing effect of ionic liquid, we chose an ionothermal method to prepare the COF-NHC. The reaction of NFB and TAB was carried out at ambient temperature and pressure for 3 h to afford a crystalline solid in 50% yields. An ionic liquid, 1-butyl-3-methylimidazoliumbis((trifluoromethyl)sulfonyl)imide ([BMIm][NTf$_2$]), was selected as both solvent and template for the Schiff base reaction [14]. Meanwhile, COF-Im with the TAB and NFB-Im as a neutral molecule and the precursor of NHC as linear block, was also prepared for comparison.

Complementary methods were employed for detailed structural characterisation of the new COF. The Fourier transform infrared (FT-IR) spectrum of COF-NHC shows a strong C=N stretch at 1635 cm^{-1}, indicating the formation of imine bonds (Figure S1) [6]. The structures of COF-Im and COF-NHC were also eventually verified by solid-state ^{13}C cross-polarisation magic angle spinning (CP-MAS) NMR spectroscopy (Figure S2). The resonance signals around 69, 129, 137 and 192 ppm were assigned to the carbon atoms of methylene, imidazole moieties and terminal aldehyde groups in the COF-Im network, respectively (Figure S2a) [6]. For the spectrum of COF-NHC (Figure S2b), the chemical shifts of 8, 20 and 49 ppm were ascribed to the propyl group, while chemical shifts from 69 to 71 ppm were attributed to the methylene carbon of propylation.

The morphology and internal structure of the COF-NHC were further obtained by scanning electron microscopy (SEM) (Figure 1a and S3), revealing a layered-sheet arrangement. Meanwhile, the boundaries in transmission electron microscopy (TEM) analysis (Figure 1c and S5) also exhibit the shape of layered-sheet arrangement. Furthermore, the high-resolution TEM (HRTEM) image reveals that COF-NHC possesses a pore structure and a degree of crystallinity as verified by the lattice fringes (Figure 1f and S6).

The crystalline structure of COF-NHC was also unambiguously confirmed by powder X-ray diffraction (PXRD) analysis. As observed in Figure S11, the as synthesised COF displays diffraction peaks, indicating the presence of crystallinity of COF-NHC. The unit cell modelling of COF-NHC was conducted based on the PXRD data in conjunction with structural simulations. The most probable structure is a typical 2D layered hexagonal network having the space group of *p6*. The nitrogen adsorption-desorption experiment at 77K (Figure 2a) resulted in a type IV adsorption isotherm, which is characteristic of a mesoporous structure. Furthermore, COF-NHC presents a pore size distribution with a mean pore width of ~2.7 nm, which is in accordance with the theoretical value of eclipsed AA stacking structure (2.8 nm, Figure 2b). Furthermore, after the geometrical energy minimization using the universal force-field implemented in the forcite module, COF-NHC in the AA stacking layers has lower total energy (Table S1 and Figure S12-13) compared to the values calculated for AB stacking models and 1-4 Å offset between the AA stacking layers. According to the experimental and the calculated PXRD patterns as well as the HRTEM images, we propose that the preferred structure of COF-NHC is an eclipsed arrangement (Rwp = 2.07% and Rp = 1.49%). The Brunauer-Emmett-Teller (BET) surface area of COF-NHC was calculated to be 45.6 m^2/g, and the total pore volume was evaluated to be 0.113 cm^3/g (P/P$_o$ = 0.99). The relatively low BET surface area is probably due to the small domains of the COF material, which is similar to that of the highly crystalline COF (Thio-COF) with low porosity (50 m^2/g)[15].

Synthesis of Pd@COF-NHC. NHC groups have strong binding interactions with metal ions in coordination chemistry, and they are a universal star ligand in catalysis. One of the most valuable applications of NHC is as a coactivator to fix metal ions into the channels of COFs. Therefore, next we explored the possibility of using COF-NHC as a carrier to fix the metal

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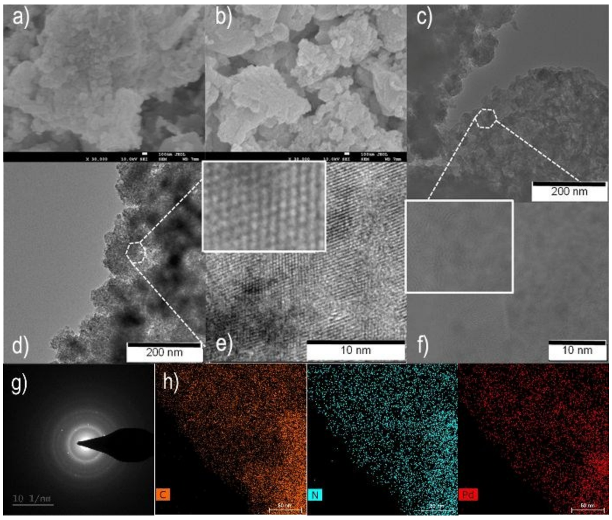

Figure 1 SEM images of (a) COF-NHC and (b) Pd@COF-NHC. TEM images of (c) COF-NHC and (d) Pd@COF-NHC. HRTEM images of (f) COF-NHC and (e) Pd@COF-NHC. Enlarged image of the lattice fringes can be observed in the inset. (g) Selected area electron diffraction (SAED) pattern. (h) EDS mapping of composition elements C, N, and Pd.

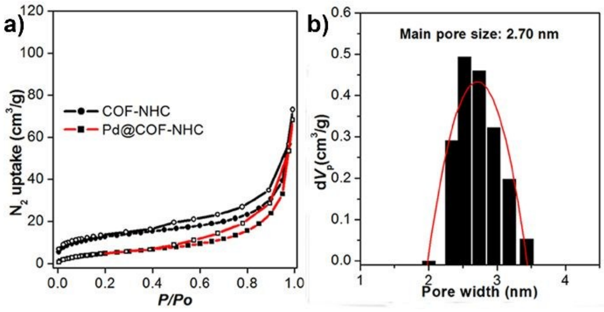

Figure 2 Nitrogen adsorption-desorption isotherm profiles of COF-NHC. (a) N_2 adsorption (filled) and desorption (open) isotherm profiles of COF-NHC and Pd@COF-NHC. (b) Pore size distribution of COF-NHC.

ions inside the pores. Through a simple post-treatment of COF-NHC with palladium acetate, a Pd(II)-complex containing COF-NHC material (Pd@COF-NHC) was effectively obtained. In order to further confirm the NHC groups are incorporated with the palladium acetate and the catalytic effect of NHC group, a reference complex Pd@COF-Im was also synthesised that was only coordinated with Pd-bearing imine ligand [8a].

Good stability of COF is an important prerequisite for application in catalysis [16]. The synthesised COF-NHC and Pd@COF-NHC material are insoluble in hot water, common organic solvents (*N*,*N*-dimethylformamide, tetrahydrofuran, dimethyl sulfoxide, and trichloromethane), acid (3M HCl), and alkali (3M NaOH). According to the thermogravimetric analysis (TGA), the COF-NHC and Pd@COF-NHC were stable up to 275 °C and 253 °C with a weight loss of 8% and 9.7%, respectively (Figure S14 and S15). The FT-IR and ^{13}C CP/MAS NMR spectra of Pd@COF-NHC were almost identical to those of COF-NHC, indicating the structural preservation of COF-NHC after the post-treatment (Figure S1 and S2). In the NMR spectrum of Pd@COF-NHC (Figure S2c), the signals at 175 and 21 ppm were attributed to the carbonyl and methyl groups of the incorporated $Pd(OAc)_2$. In comparison with the uncoordinated COF-NHC, the ^{13}C chemical shift for carbene in the NHC was displaced toward the low-field by approximately 28 ppm, which was ascribed to the effect of NHC ligand coordinated with Pd. In the typical SEM images (Figure 1b and S4), the layer-sheet structure of COF-NHC was unchanged after treatment with palladium acetate. The well-dispersed palladium species are clearly observed in the TEM images in Figure 1c and 1d. Furthermore, the HRTEM images of Pd@COF-NHC reveal that the Pd species are in a crystalline phase, as demonstrated by the clear lattice fringes (Figure 1e and S8). Meanwhile, the corresponding selected area electron diffraction (SAED) pattern in Figure 1g shows the polycrystalline nature of Pd and characteristic diffraction rings[15]. Furthermore, the composition of Pd@COF-NHC was characterised by energy dispersive spectrum (EDS) elemental mapping. As shown in Figure 1h, the component elements Pd, C, and N are all evenly distributed in the polymer material, again supporting the excellent dispersity of Pd in the COF-NHC carrier. The result of HRTEM also implies a clean one-dimensional channel. The porosity and surface areas were measured at 77K (Figure 2c). The BET surface area of Pd@COF-NHC was approximately 18.8 m^2/g. Its total pore volume (0.106 cm^3/g, $P/P_o = 0.99$), main pore size (2.7 nm) and adsorption isotherm (type IV) were not significantly changed with respect to the unmodified COF-NHC framework. In comparison with COF-NHC, Pd@COF-NHC showed a large decrease in the BET surface area and similar pore volume and pore size distribution, taken together, indicated that the Pd species did not block the cavities [6].

The coordination state of the anchored palladium within Pd@COF-NHC was studied by X-ray photoelectron spectroscopy (XPS) measurements. As shown in Figure 3 and S16, two peaks related to Pd 3d5/2 and 3d3/2 are centred at the binding energies of 337.9 and 341.1 eV, respectively. These binding energies are the features of divalent Pd cations and also consistent with the values reported for Pd(II)-NHC complex [4c, 17]. Furthermore, inductively coupled plasma mass spectrometry (ICP-MS) data show the Pd content in the composite material to be 20.1 wt %, which is in good agreement with the theoretical value (20.3 wt %),

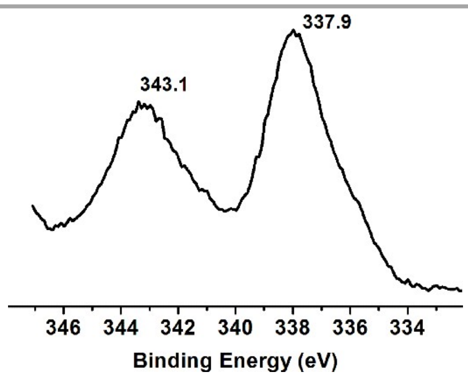

Figure 3 Pd 3d XPS spectra of Pd@COF-NHC.

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corresponding to ~1 Pd atom per unit cell (Scheme 1). These observations suggest the excellent confinement ability of the COF-NHC material.

Catalytic properties of Pd@COF-NHC

Catalysis of Suzuki-Miyaura reaction

High catalytic activity. The catalytic activity of Pd@COF-NHC was firstly examined in Suzuki-Miyaura coupling reaction, are presentative Pd-catalysed reaction [9].

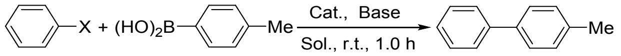
The initial reaction conditions were optimised using halobenzene and 4-chlorophenylboronic acid as raw materials and COF-NHC with palladium as catalyst (Table 1 and S3). In the cross coupling of chlorobenzene and phenylboronic acid, the ligand COF-Im, without the NHC group in its framework provided a 33% yield after 1 h at room temperature (see Table 1, entry 1). When the ligand COF-NHC was employed, the yield was dramatically improved to 85% (see Table 1, entry 2). One important observation was that the homogeneous catalyst and post synthesised Pd@COF-NHC had very similar catalytic activity, with the respective yields of 79% and 78% (Table 1, entries 2-3). Furthermore, bromobenzene and iodobenzene afforded excellent yield with complete selectivity of biphenyl (Table 1, entries 4-5). Considering the universality and activity of different halobenzenes, the bromobenzene was chosen as the model substrate to optimise the reaction condition. Different amounts of catalyst (1 mol%, 0.5 mol%, 0.25 mol% Pd contents) were investigated and the highest catalytic activity was observed using 0.5mol% (Table S3, entries 4, 6-7). The catalytic activity of Pd@COF was only slightly affected by the base, and K_2CO_3 was selected for the weak causticity (Table S3, entries 6-11). The cross-coupling reaction could occur readily in aqueous solution at ambient temperature within about 1.0 h. Notably, the cross-coupling reactions with 99% yield in the presence of Pd-based COF materials at room temperature have not been reported in the literature.

To explore the scope of the cross-coupling reaction, a variety of substituted aryl halides were reacted with different substituted phenylboronic acids using the optimised conditions (Table 2, entries 1-11). Under the selection condition, the presence of a substituted group of aryl bromide was tolerated with excellent yields (Table 2, entries 1-9). Reactions with electron-withdrawing substituents on the bromobenzene led to relatively higher yields, while electron-donating substituents on the phenylboronic acid only gave slightly lower yields. Compared with aryl bromide, the reaction of aryl iodide generated a higher yield (Table 2, entries 10-11), which is due to the relatively higher activity of iodide. In comparison with the Pd-N containing COF (COF-LZU1, entry 12), Pd@COF-NHC could be carried out under greener and gentler conditions, such as non-organic solvent, shorter reaction time, and no heating while maintaining the same reaction yield. This result indicated that the stronger σ-donating ability of NHC increased the activity of Pd catalyst.

Recyclability of catalyst

The kinetics of the coupling reaction between 1-bromo-4-nitrobenzene and phenylboronic acid using 0.5 mol% Pd@COF-NHC catalyst at room temperature was investigated. The reaction showed a sigmoidal kinetic curve, with the highest catalytic activities during the first 0.5 h (Figure 4).

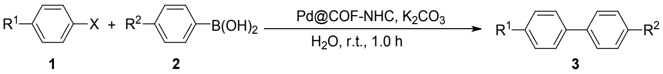
Table 1 Optimisation Studies of Suzuki-Miyaura Cross Coupling[a]



Entry	Catalyst Ligand	Pd [b]	X	Solvent	Yield(%) [d]
1	COF-Im	$Pd(OAc)_2$	Cl	MeOH	33
2	COF-NHC	$Pd(OAc)_2$	Cl	MeOH	79
3	Pd@COF-NHC [c]		Cl	MeOH	78
4	Pd@COF-NHC [c]		Br	MeOH	99
5	Pd@COF-NHC [c]		I	MeOH	99
6	Pd@COF-NHC [c]		Br	H_2O	99

[a] Reaction condition: halobenzene (0.50 mmol), 4-chlorophenylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), solvent (2.5 mL), room temperature, 1.0 h; [b] $Pd(OAc)_2$ (0.5 mol%); [c] Pd@COF-NHC (0.5 mol%); [d] Isolated yields.

Table 2 Suzuki-Miyaura Cross Coupling of Aryl Halide with Different Boronic Acids [a]



Entry	R_1	R_2	X	Products	Yield(%) [b]
1	H	H	Br	**3a**	99
2	CH_3	H	Br	**3b**	97
3	OCH_3	H	Br	**3c**	95
4	NO_2	H	Br	**3d**	99
5	CH_3	Cl	Br	**3e**	90
6	NO_2	Cl	Br	**3f**	99
7	H	Cl	Br	**3g**	99
8	H	CH_3	Br	**3b**	99
9	H	OCH_3	Br	**3c**	95
10	H	H	I	**3a**	99
11	CH_3	H	I	**3b**	99
12[c]	NO_2	H	Br	**3d**	97

[a] Reaction condition: Ar-X (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), Pd@COF-NHC (0.5 mol%), solvent (2.5 mL, H_2O), room temperature for 1.0 h; [b] Isolated yields; c Results from ref 6 (0.5 mol% Pd/COF-LZU1 was used, *p*-xylene as solvent, 150 °C, 5h).

A “hot filtration” experiment was also performed to confirm that the reaction occurred through heterogeneous rather than homogeneous catalysis. In the absence of reactants, the mixture of Pd@COF-NHC, water and sodium carbonate was stirred for 1.0 h. The filtrate from the hot mixture was then used to catalyse the reaction of phenylboronic acid and *p*-nitrobromobenzene. No conversion could be observed. In another test, the reaction was carried

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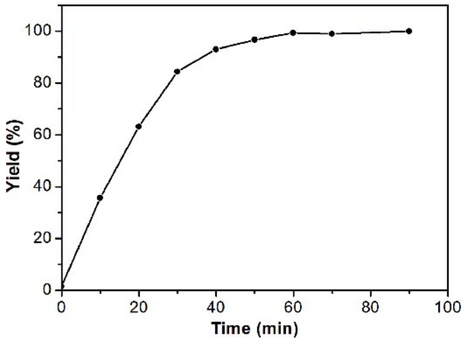


Figure 4 Yield-time curve for the Suzuki coupling reaction.

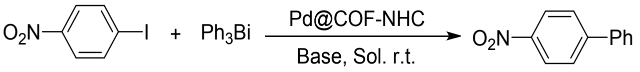
out for 0.15 h, and the catalyst was immediately removed by filtration from the hot reaction mixture (with a yield of 46.9%). Then, the filtrate was kept under the reaction condition for another 1.0 h and 4.0 h, and the final conversion changed very little (to 47.5 % and 48.6%, respectively). Furthermore, the ICP-AES analysis showed that the palladium concentration in the filtrate was lower than 1 ppm (0.05% of the Pd content). Hence, almost no palladium was leached into the solution owing to the strong bond between NHC and palladium, and the catalytic activity of the Pd@COF-NHC mainly came from the palladium complex.

The separation and recyclability of noble metal catalysts are trends in the catalysis industry, along with the development of green chemistry. Pd@COF-NHC was directly reused after being separated from the reaction through centrifugation and washing with water and acetonitrile without any other post-treatment. Its stability and reusability were further assessed using 0.5 mol% catalyst in the cross-coupling reaction of *p*-nitrobromobenzene with phenylboronic acid (Table S4). The results indicate that this catalyst could be reused at least eight times without obviously loss of catalytic activity, indicating its ultra-stable property. The structure of Pd@COF-NHC catalyst after the 8th cycle was examined by TEM and XPS. The TEM image shows no obvious change in the size of Pd@COF-NHC, and the palladium species was still highly dispersed (Figure S17). Meanwhile, the XPS spectra show the palladium was still +2 state (Figure S18). We infer that the excellent activity of Pd@COF-NHC catalyst is probably due to the unique coordination mode of COF-NHC. The eclipsed layered-sheet arrangement of COF-NHC forms channels, which provide efficient access to the active sites and fast diffusion for the reagents and products. Therefore, the bidentate NHC and imine hybrid ligands not only increased catalyst activity but also firmly embedded the Pd species into COF channels to create highly dispersed palladium at the atomic level.

Catalytic activity for the C-C cross coupling of triarylbismuths with aryl halide

After establishing a new and efficient catalytic system using Pd@COF-NHC for the traditional Suzuki-Miyaura coupling reaction under mild condition, we turned our attention to the carbon-carbon coupling reactions with triarylbismuths as reagents, since the organobismuth compounds are environmentally benign [18]. The initial reaction conditions were optimised using 4-iodonitrobenzene and triphenyl-bismuth as

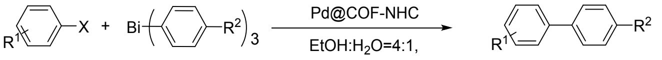
Table 3 Optimization Studies on the crosscoupling of 4-iodonirtobenzene with $BiPh_3$ [a]



Entry	Solvent	Yield (%)[b]
1	DMSO	56
2	$EtOH:H_2O=4:1$	96

[a] Reaction condition: 4-iodonitrobenzene (1 mmol), triphenyl-bismuths (0.43 mmol), K_2CO_3 (4 mmol), solvent (2.5 mL), Pd@COF-NHC (2 mol%) room temperature for 5.0 h; [b] Isolated yields.

Table 4 The crosscoupling reaction of triarylbismuths and aryl halides [a]



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Entry	X	R_1	R_2	Products	Yield (%) [b]
1	I	3-NH_2	H	**3h**	89
2	I	4-NH_2	H	**3i**	86
3	I	4-OCH_3	H	**3c**	85
4	I	4-CH_3	H	**3b**	91
5	I	Cl	H	**3g**	94
6	I	4-CN	H	**3j**	94
7	I	4-NO_2	H	**3d**	96
8	I	4-NO_2	4-CH_3	**3k**	82
9	I	4-CN	4-CH_3	**3l**	86
10	I	4-CH_3	4-CH_3	**3m**	93
11	I	4-OCH_3	4-CH_3	**3n**	80
12	I	4-CH_3	4-OCH_3	**3o**	85
13	I	3-NH_2	4-CH_3		89
14	I	4-NO_2	4-OCH_3	**3p**	90
15	I	4-CN	4-OCH_3	**3q**	85
16	I	4-OCH_3	4-OCH_3	**3r**	89
17	I	3-NH_2	4-OCH_3	**3s**	92
18	I	4-NH_2	4-OCH_3	**3t**	95
19	Br	4-NO_2	4-CH_3	**3k**	14
20	Br	4-NO_2	4-CH_3	**3k**	95
21[c]	Br	4-NO_2	H	**3d**	93
22[c]	Br	4-NO_2	4-OCH_3	**3p**	92
23[c]	Br	4-CN	H	**3j**	93
24[c]	Br	H	4-CH_3	**3b**	94
25[c]	Br	4-CH_3	4-CH_3	**3m**	91
26[c]	Br	4-OCH_3	H	**3c**	92

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27[c]	Br	4-OCH_3	4-CH_3	**3n**	95
28[c]	Br	4-OCH_3	4-OCH_3	**3r**	90

[a] Reaction condition: aryl halides (1 mmol), triaylbismuths (0.43 mmol), K_2CO_3 (4 mmol), solvent (2.5 mL, EtOH:H_2O = 4:1), Pd@COF-NHC (2 mol%) room temperature for 5.0 h; [b] Isolated yields; [c] Reflux.

a template under different bases and solvents at room temperature (Table S5, entries 1-18; Table 3). As shown in Table S3, reactions of 4-iodonitrobenzene with $BiPh_3$ in DMSO under different bases led to the corresponding 4-nitrobiphenyls in 21-56% yields, with K_2CO_3 gaving the higher yield (Table 3, entry 1; Table S5, entries 1-5). The catalytic activity of Pd@COF-NHC was highly dependent on the solvent and reaction time. Reported cross-coupling reactions of triarylbismuths with aryl halides were conducted in expensive dry solvents such as NMP, DME, or DMSO [9a]. In contrast, Pd@COF-NHC allows the reactions to progress in ethanol aqueous solution at room temperature within 5.0 h, making it a greener system (Table 3, entry 2; Table S5, entries 14-18). Therefore, the ethanol aqueous solution was selected as the optimal solvent.

Using the optimised conditions, the cross-coupling scope and generality were investigated with a variety of aryl iodides and triarylbismuths in ethanol aqueous solution at room temperature for 5.0 h (Table 4, entries 1-19). As shown in Table 4, the excellent catalytic activity of 2 mol% Pd loaded on COF-NHC was observed under mild conditions regardless of the presence of electron-withdrawing or electron-donating groups on phenyl (80-96%). Additionally, the aryl bromides also gave excellent yield under higher temperatures with a remarkably broad substrate scope (Table 4, entries 20-28).

Conclusions

We have developed the *N*-heterocyclic carbene containing imine-linked COF and used it to synthesis a stable and atomically dispersed palladium heterogeneous catalyst (Pd@COF-NHC). The catalyst exhibited superior activities in Suzuki-Miyaura coupling reaction at room temperature in aqueous media with high yield and broad scope, and can be reused directly at least eitht times without obvious loss of catalytic activity. Meanwhile, the C-C coupling reactions of aryl halides with arylbismuths can be performed in unprecedented mild conditions for high yields. The structure characterisation result of Pd@COF-NHC suggests that the palladium is likely to be fixed firmly in the pores of the COF-NHC framework through imine-metal-NHC (N-Pd-C) binding interactions, preventing the Pd ions from aggregation and leaching. This work presents new insights into using functional COFs as heterogeneous catalysts in organic synthesis and green chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by Natural Science Foundation of Science and Technology Agency of Shanxi Province (201801D221068), the Natural Science Foundation of Shanxi Normal University (ZR1708), and 1331 Project of Shanxi Province.

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DOI: 10.1039/C9GC01993F

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An *N*-Heterocyclic Carbene Functionalized Covalent Organic Framework: Atomically Dispersed Palladium Catalyst for Coupling Reactions under Mild Condition

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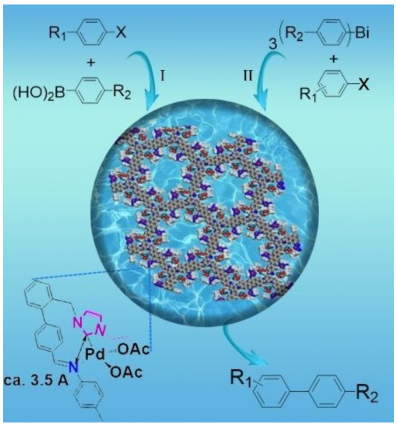

We report a heterogeneous catalyst of atomically dispersed palladium complex based on *N*-heterocyclic carbene functionalized covalent organic framework, which show highly activity in the carbon-carbon cross coupling reaction of arylboronic acid/triarylbismuths with aryl halides at room temperature in pure/ethanol aqueous solvent for multi-reused.