

Article

Nitrogen ligands in two-dimensional covalent organic frameworks for metal catalysis



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1. Introduction

ABSTRACT

We introduced bipyridine ligands into a series of two-dimensional (2D) covalent organic frameworks (COFs) using 2,2'-bipyridine-5,5'-dicarbaldehyde (2,2'-BPyDCA) as a component in the mixed building blocks. The framework of the COFs was formed by the linkage of imine groups. The ligand content in the COFs was synthetically tuned by the content of 2,2'-BPyDCA, and thus the amount of metal, palladium(II) acetate, bonded to the nitrogen ligands could be manipulated. Both the bipyridine ligands and imine groups can coordinate with Pd(II) ions, but the loading position can be varied, with one ligand favoring binding in the space between adjacent COFs' layers and the other ligand favoring binding within the pores of the COFs. The Pd(II)-loaded COFs exhibited good catalytic activity for the Heck reaction.

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An emerging class of porous materials is covalent organic frameworks (COFs) made up of light weight elements (e.g., B, C, H, N, O) [1–4]. COFs have been investigated extensively in recent years because of their potential applications in a number of areas, including catalysis [5–9], gas storage/separation [10–14], sensing [15,16] and energy conversion [17–24]. COFs can be synthesized using the general principles of reticular chemistry where organic building blocks with pre-designed geometries and radicals are linked together by the formation of covalent bonds to give an extended periodic network. The general features of this strategy allow for the flexible control of pore parameters (e.g., size, shape, volume, distribution) and also favor the introduction of functional active sites onto the skeleton of the COFs. As a result, COFs, which are also known as

"organic zeolites", are widely recognized as promising supports for the immobilization of catalysts for use in organic synthesis.

2D COFs are easier to prepare than their 3D counterparts because of their structural simplicity [25–29], and they have therefore been explored in much greater detail for their application to catalysis [5–8]. Consideration of a typical 2D COF structure reveals that the covalently bonded planar sheets are stacked together by π – π interactions leading to the formation of eclipsed or staggered columnar arrays [1]. This vertical alignment of COFs leads to the formation of one-dimensional (1D) open channels, which can significantly enhance the diffusion of substances and also be used to support catalysts through the modification of the skeleton of the COFs [6,30]. Furthermore, although classical boroxine- and boronate-ester-based COFs are sensitive to moisture [31,32], the more recently developed COFs derived from nitrile trimeriza-

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tion [33] and Schiff-base [34–36] reactions exhibit much better stability at high temperatures and in a range of different solvents, making them useable at standard catalytic conditions. In general, 2D imine-type (i.e., Schiff-base) COFs that incorporate Pd ions or Pd nanoparticles have shown superior catalytic performance in C–C coupling reactions than conventional Pd catalysts [5,8]. The strong coordination effect between the imine ligands and noble metal leads to negligible levels of catalyst leaching after repeated catalytic cycles. Furthermore, given that the imine groups can be uniformly distributed throughout the COFs, their one-to-one interaction with the catalyst allows for the isolation of the active sites of the catalyst at a molecular level [37]. This level of uniform dispersion is not easy to achieve with conventional porous supports.

Several reports have been published on the application of 2D imine-linked COFs as catalyst carriers, where the imine groups were used to bind metallic guests [5,8]. Given that the density of the imine groups within a certain COF is usually constant, it is challenging to manipulate the amount of catalyst on the surface of the support. With this in mind, it was interesting to introduce different nitrogen ligands into the COFs simultaneously and regulate their contents to allow for controllable metal loading. Bipyridine units have recently been incorporated at the pore edge of metal organic frameworks (MOFs) [37,38] and COFs [30]. The versatile combination of these nitrogen ligands with metallic components is well recognized in coordination chemistry. As a result, bipyridine units can be used as a second type of nitrogen ligand that can be used in conjunction with imine type ligands in the skeleton of the COFs.

Here, we report the development of a novel procedure for the control of the nitrogen content of the ligands in 2D COFs using a pore surface engineering strategy [39]. Imine and bipyridine groups were both included in the skeleton of the COFs to allow for controllable metal loading. These two types of nitrogen ligands can both coordinate palladium(II) acetate (Pd(OAc)₂), but the loading position of the Pd(OAc)₂ can be varied. The imine ligand favors binding Pd(OAc)₂ in the space between adjacent layers of the COFs, while the bipyridine ligand would coordinate Pd(II) in the pores of the COF. The catalytic performances of these COFs were investigated and the results indicated that the Pd(II)-based COF exhibited good catalytic efficiency for the Heck reaction.

2. Experimental

2.1. Materials

All the reagents were used as received without further purification. 1,3,6,8-tetrabromopyrene, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 4-formylphenylboronic acid, 4,4'-biphenyl dialdehyde, Pd(OAc)₂, and tetrakis(triphenylphosphine) palladium(0) were purchased from TCI Chemicals. 5,5'-dimethyl-2,2'-dipyridyl, tert-butoxy bis(dimethylamino)methane, and benzidine dihydrochloride were purchased from Aldrich. Iodobenzene, 4-iodotoluene, 4-iodoanisole, 4-iodobenzonitrile, and 1,4-diiodobenzene were purchased from Aladdin. Mesitylene, dioxane, acetic acid, dimethylacetamide, tetrahydrofuran, acetone, dichloromethane, methanol, ether, chloroform, *N*,*N*-dimethylformamide, toluene, styrene, hexadecane, hydrochloric acid, fuming nitric acid, potassium carbonate, anhydrous magnesium sulphate and sodium periodate were purchased from Sinopharm Chemical Reagent Co.

2.2. Synthesis

Synthesis of the building blocks. 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline (PyTTA) [30], 2,2'-bipyridine-5,5'-dicarbaldehyde (2,2'-BPyDCA) [40], and 1,3,6,8-tetrakis(4formylphenyl) pyrene (TFPPy) [41] were prepared according to literature reports.

Synthesis of 25% BPy COF. 2,2'-BPyDCA (16 mg, 0.075 mmol), 4,4'-biphenyl dialdehyde (47 mg, 0.225 mmol) and PyTTA (85 mg, 0.15 mmol) were placed in a glass ampule vessel (20 mL), followed by adding a solution of mesity-lene/dioxane/3 mol/L acetic acid (3/3/1 by volume; 3.5 mL). The mixture was sonicated for 5 min and then flash frozen in liquid nitrogen. The vessel was evacuated to a pressure of ~20 Pa, flame-sealed, and heated at 120 °C for 3 d. The resulting precipitate was washed sequentially with tetrahydrofuran (3 times) and acetone (3 times) to give a powder. This was dried at 120 °C under vacuum for 12 h to give the desired product in 88% yield. Elemental analysis (%) calcd. for $(C_{67}H_{41}N_5)_n$: C 87.9; H 4.5; N 7.6; Found: C 82.2; H 4.7; N 6.8.

Synthesis of 50% BPy COF. This material was synthesized in the same way as the 25% BPy COF, except for the feed ratio of the two dialdehydes: 2,2'-BPyDCA (31 mg, 0.15 mmol) and 4,4'-biphenyl dialdehyde (31 mg, 0.15 mmol). The product was isolated as a powder in 88% yield. Elemental analysis (%) calcd. for $(C_{66}H_{40}N_6)_n$: C 86.5; H 4.4; N 9.1; Found: C 80.9; H 4.5; N 7.8.

Synthesis of 75% BPy COF. This material was synthesized in the same way as the 25% BPy COF, except for the feed ratio of the two dialdehydes: 2,2'-BPyDCA (47 mg, 0.225 mmol) and 4,4'-biphenyl dialdehyde (16 mg, 0.075 mmol). The product was isolated as a powder in 83% yield. Elemental analysis (%) calcd. for $(C_{65}H_{39}N_7)_n$: C 85.1; H 4.2; N 10.7; Found: C 78.7; H 4.5; N 9.1.

Synthesis of 100% BPy COF. This material was synthesized in the same way as the 25% BPy COF, except for the feed ratio of the two dialdehydes: 2,2'-BPyDCA (64 mg, 0.30 mmol) and 4,4'-biphenyl dialdehyde (none). The product was isolated as a powder in 76% yield. Elemental analysis (%) calcd. for $(C_{64}H_{38}N_8)_n$: C 83.7; H 4.1; N 12.2; Found: C 74.8; H 4.7; N 10.3.

Synthesis of Pd(II)@X% BPy COF. Pd(OAc)₂ was incorporated into *X*% BPy COFs using a simple solution infiltration method [5,8]. The resulting composites were named Pd(II)@X% BPy COFs. In a typical procedure, *X*% BPy COFs (0.03 mmol, calculated using the framework repeating unit) was treated with a solution of Pd(OAc)₂ in dichloromethane (15 mL). The resulting suspension was stirred at room temperature for 12 h. The precipitate was washed with excess dichloromethane to remove any dissociated Pd(OAc)₂ and then dried at 120 °C under vacuum for 12 h to give Pd(II)@X% BPy COFs.

Pd(OAc)₂ was added in excess and the exact fed amount was adjusted based on the total nitrogen content of the COFs. Pd(OAc)₂ was dosed as follows: 28 mg, 0.12 mmol (X = 25); 33 mg, 0.15 mmol (X = 50); 39 mg, 0.17 mmol (X = 75); and 44 mg, 0.20 mmol (X = 100).

2.3. Procedure for the Heck reaction

A mixture of aryl iodide (204 mg, 1.0 mmol), styrene (120 mg, 1.1 mmol), potassium carbonate (276 mg, 2.0 mmol) and N.N-dimethylformamide (5 mL) was stirred and purged with N₂. Pd(II)@X% BPy COFs were then added as catalyst (5 mg, containing slightly less than 0.01 mmol of Pd element). The resulting mixture was heated at 105 °C under reflux for 5 h. The mixture was then cooled to ambient temperature and filtered, and the solid (catalyst and potassium carbonate blend) was washed with dichloromethane (3 × 10 mL). The combined filtrates were washed with water (20 mL). The separated organic phase was concentrated under vacuum at 90 °C to give a slurry, which was mixed with water (20 mL) to precipitate the crude product. This powder sediment was filtered and recrystallized from chloroform to give the pure product. Iodobenzene was selected as the substrate for the recyclability tests with Pd(II)@75% BPy COF as the catalyst. The catalyst was removed by filtration after each cycle together with the K₂CO₃, which was removed by washing with water. The catalyst was then dried under vacuum at 120 °C and reused for another round of catalysis.

2.4. Characterization

Elemental analysis was performed by an organic elemental analyzer (vario MACRO cube, Elementar, Germany). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted by ICP-OES 7300DV (PerkinElmer). The sample was firstly calcined at 1000 °C in air for 12 h to burn off organic moieties. The residue was dissolved by aqua regia and then diluted by water for ICP-OES testing. Fourier transform infrared (FT-IR) measurements were carried out on a Bruker spectrophotometer (Model TENSOR27) with powder pressed KBr pellets. Powder X-ray diffraction (PXRD) analysis was carried out on a Rigaku RINT D/Max 2500 powder diffraction system, using a Cu K_{α} radiation ($\lambda = 0.15432$ nm). Thermogravimetric analysis (TGA, STA449F3, NETZSCH, Germany) was performed from room temperature to 750 °C at a heating rate of 10 °C/min and a N2 flow rate of 20 mL/min. The nitrogen physisorption experiment was conducted at -196 °C on a QUADRASORB SI gas sorption system (Quantachrome Instruments). The sample was degassed at 120 °C under vacuum before testing. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was evaluated by the nonlocal density function theory (NLDFT) method. The morphology of sample was observed by a transmission electron microscope (TEM, Tecnai G2 F30, FEI Company, operating at 120 kV). X-ray photoelectron spectroscopy (XPS) was recorded by an ESCALAB 250Xi equipped with Al K_{α} radiation (1486.6 eV, 200 W) on a sample powder

pressed pellet. Gas chromatography (GC, Agilent 7890A) was used to monitor the conversion in the reaction using hexadecane as an internal standard and dichloromethane as solvent. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded by a Bruker Advance III 400 MHz NMR spectrometer (Bruker BioSpin Corporation, Fällanden, Switzerland).

3. Results and discussion

Two dialdehyde monomers, namely 2,2'-BPyDCA and 4,4'-biphenyl dialdehyde, were chosen as the building blocks to adjust the nitrogen content of the 2D COFs (Scheme 1). These two monomers were blended together in different molar ratios and reacted with PyTTA using a Schiff-base condensation [30]. Four different 2D imine-linked COFs were synthesized and named as X% BPy COF (X = 25, 50, 75, 100), where X% represented the molar percentage of 2,2'-BPyDCA present in the dialdehyde blend. The density of the imine groups in the 2D COFs was constant, but the number of bipyridine moieties on the wall of the pores was varied by the feed ratio of the 2,2'-BPyDCA monomer.

FT-IR spectra of the four *X*% BPy COFs showed a C=N stretching vibration at 1622 cm⁻¹ (Fig. 1), which indicated the successful formation of the imine linkage. The PXRD patterns of the *X*% BPy COFs revealed that there were negligible difference in the crystalline structure. Diffraction peaks were observed at $2\theta = 3.2^{\circ}$, 4.6°, 6.4°, 9.7°, 12.9° and 23.8°, which were attributed to the (110), (020), (220), (330), (440) and (001) facets, respectively (Fig. 2). The use of lattice modeling and the Pawley refinement process led to an eclipsed AA stacking model that could reproduce the PXRD results in peak position and intensity. These results showed that the *X*% BPy COFs belonged to the P₂₁₂₁₂ space group with the unit cell parameters of *a* = 4.214



Scheme 1. Pore surface engineering strategy used to modulate the nitrogen content of the 2D imine-type COFs.



Fig. 1. FTIR spectra of *X*% BPy COFs (*X* = 25, 50, 75, 100).

nm, *b* = 3.690 nm, *c* = 0.374 nm and $\alpha = \beta = \gamma = 90^{\circ}$. These modeling results were in good agreement with the experimental profiles and gave R_{wp} and R_p values of 6.27% and 4.74%, respectively. An alternative AB staggered model did not match the observed data. Elemental analysis confirmed that the nitrogen content of the *X*% BPy COF was proportional to the feed ratio of 2,2'-BPyDCA, and that it could be tuned in the range of 6.8 wt% to 10.3 wt% (Fig. 3). The nominal nitrogen content was higher than the measured value due to residual organic solvent or adsorbed H₂O in the pores [34]. It is noteworthy that the reaction of only 4,4'-biphenyl dialdehyde with PyTTA under the same conditions did not result in the formation of



Fig. 2. (a) PXRD patterns of 100% BPy COF: experimental ((1), red line) Pawley refined ((2), green dotted line) difference between experimental and calculated data (3), calculated for AA-stacking (4) and AB-stacking (5); (b) Unit cell structure of 100% BPy COF using the AA stacking model along the *z* axis; (c) Unit cell structure of 100% BPy COF using the AA stacking model along the *y* axis; (d) Unit cell structure of 100% BPy COF using the AB stacking model along the *z* axis; (e) Unit cell structure of 100% BPy COF using the AB stacking model along the *y* axis.

well-defined crystalline COFs (named BiPh COFs), which suggested that the addition of 2,2'-BPyDCA was activated and acted in concert with 4,4'-biphenyl dialdehyde during the formation of the COFs to give well-defined crystalline structures [42]. The synthesized X% BPy COFs were insoluble in water and a range of common organic solvents. TGA curves of the different X% BPy COFs revealed they were highly stable, with decomposition temperatures of almost 500 °C (Fig. 4). These results revealed that the COFs would be good catalysts or catalyst carriers for catalytic applications. The porous properties of the COFs were characterized to give the BET surface areas of 538, 1554, 1438 and 1288 m²/g for *X* values of 25, 50, 75 and 100, respectively, with pore sizes of 2.6 or 2.7 nm. TEM images revealed clear 1D channels with a diameter of 2 nm (Fig. 5(a)), which provided further demonstration of the formation of well-ordered mesoporous pores.

It was well known that imine and bipyridine units can both coordinate with a variety of noble metals (e.g., Pd, Pt, Rh, Ru and Ir). As a readily available catalyst for organic synthesis, Pd(OAc)₂ was selected as the model system to be incorporated into the different *X*% BPy COFs using a simple solution infiltration method. The resulting composites are referred to as Pd(II)@*X*% BPy COFs. It was envisaged that the formation of a strong interaction between the Pd(II) complex and the nitrogen ligands would lead to the immobilization of Pd(OAc)₂ on the COFs. The TEM image revealed that there was very little aggregation of Pd(OAc)₂ to block the channels of the COFs (Fig. 5(b)). The thermal stability of the COFs was also well preserved following the loading of the Pd(OAc)₂. XPS was performed to



Fig. 3. Elemental analysis of the nitrogen content in the X% BPy COFs.



Fig. 4. TGA curves for the X% BPy COFs.



Fig. 5. TEM images of (a) 75% BPy COF and (b) Pd(II)@75% BPy COF.

determine the coordinated position of Pd(OAc)₂ (Fig. 6). Free Pd(OAc)₂ showed a characteristic peak for Pd(II) $3d_{5/2}$ at 338.3 eV. This peak was negatively shifted to 337.9 eV when Pd(OAc)₂ was coordinated to a 2,2'-BPyDCA monomer. The bipyridine-free BiPh COF mentioned above contained only imine groups, and the coordination of these groups to Pd(OAc)₂ resulted in a signal at 337.7 eV. In contrast, all four of the Pd(II)@X% BPy COFs gave a Pd(II) $3d_{5/2}$ peak at 337.8 eV, which indicated that the bipyridine and imine groups were both involved in the binding of Pd(OAc)₂.

The nominal maximum Pd loading was calculated to have a quasi-linear relationship with the total amount of nitrogen ligands (Fig. 7). However, the measured values were lower than these nominal values and did not give a linear relationship with the total nitrogen content of the ligands (Fig. 7). Higher Pd contents were found in Pd(II)@50% BPy COF (18.2 wt% Pd element) and Pd(II)@75% BPy COF (18.7 wt% Pd element). From consideration of the BET surface areas, it was likely that the structural regularity of the COF scaffolds had an impact on the loading of Pd(OAc)₂. The insufficient occupation of the nitrogen ligands with Pd(OAc)₂ (with a molecular size of $1.06 \times 0.5 \times 0.43$ nm [43]) was probably caused by steric limitation since the individual sheets of the 2D COFs were stacked in an eclipsed mode with an interlayer distance of 0.374 nm (Fig. 2).



Fig. 6. XPS results (Pd 3*d*) for the samples showing the coordination of Pd(OAc)₂. Pure Pd(OAc)₂ and the complex formed between Pd(OAc)₂ and 2,2'-BPyDCA (Pd(II)@2,2'-BPyDCA) were tested for comparison.



Fig. 7. Nominal and measured Pd loading in the Pd(II)@X% BPy COFs.

This would have resulted in the balancing of the ligand content and the surface area of the COFs to give the optimum loading. The Pd(II)@X% BPy COFs gave different Pd loadings in the range of 14.3 to 18.7 wt%, which are among the highest reported values with a similar porous polymer matrix [44]. Although the Pd(II)@X% BPy COFs still have mesoporous pores, their BET surface areas were decreased significantly to 283, 982, 847 and 731 m²/g and the pore diameter of the COFs decreased to 2.3, 2.2, 2.1 and 2.0 nm, respectively, for X values of 25, 50, 75 and 100 because of the presence of the guest molecules. To further elucidate the coordination position of the Pd(OAc)₂ molecules, another bipyridine-free 2D imine-type COF, named as TF-BD COF, was also synthesized. TF-BD COF can be regarded as the analogue of the BiPh COF as the TF-BD COF has a similar structure to BiPh COF but with much better crystallinity. The TF-BD COF showed negligible change in its pore size both before (2.6 nm) and after (2.6 nm) the loading of Pd(OAc)₂. This result indicated that the Pd(OAc)₂ molecules were coordinated to the imine groups located between adjacent COF sheets, since they did not have an influence on the pore diameter [5]. In contrast, the Pd(OAc)₂ molecules coordinated to bipyridine groups occupied the pore space, and therefore led to a reduction in pore size (Fig. 8) [30]. As the percentage of bipyridine units in the COFs increased, their loading ratio with Pd(OAc)₂ also increased, which led to the gradual decrease in the pore size.

To characterize the catalytic performance of the COFs, the Pd(II)@X% BPy COFs were used as heterogeneous catalyst for the classical Heck reaction, which is a powerful and versatile



Fig. 8. Scheme for the regulated Pd(OAc)₂ coordination on bipyridine and imine groups.

Table 1

The series of Pd(II)@X% BPy COFs catalysts for the Heck reaction.

R	→-ı +	Pd(II)@X%	⁶ BPy COF →	/──⟨──⟩──R
Entry	<i>X</i> %	R	Conversion ^a (%)	Yield ^b (%)
1	25	Н	98	92
2	50	Н	99	94
3	75	Н	99	96
4	100	Н	99	95
5	25	CH_3	98	93
6	50	CH_3	99	95
7	75	CH_3	99	96
8	100	CH_3	99	95
9	25	OCH_3	95	90
10	50	OCH_3	97	93
11	75	OCH ₃	97	94
12	100	OCH_3	96	91
13	25	CN	79	73
14	50	CN	80	77
15	75	CN	83	80
16	100	CN	81	76
17	25	Ι	92	88
18	50	Ι	94	91
19	75	Ι	96	92
20	100	Ι	95	90

Reaction conditions: aryl iodide (1.0 mmol), styrene (1.1 mmol), potassium carbonate (2.0 mmol), Pd(II)@X% BPy COF (5 mg, containing about 0.01 mmol of Pd), *N*,*N*-dimethylformamide (5 mL), 105 °C, 5h, N₂ protection. A larger charge of styrene (2.2 mmol) was added when 1,4-diiodobenzene containing twice as many functional groups was used as substrate. ^a Monitored by gas chromatography using hexadecane as an internal standard and dichloromethane as a solvent. ^bIsolated yield.

method for the synthesis of arylated alkenes. A model reaction between aryl iodide and styrene was selected and carried out under general C–C coupling reacting conditions [8,37]. All the Pd(II)@X% BPy COFs exhibited high catalytic efficiency for the Heck reaction of a variety of different substrates and gave the desired products in high yields. The results of these reactions are summarized in Table 1. Kinetic studies also showed a large



Fig. 9. Reaction kinetics of Pd(II)@75% BPy COF as catalyst in the Heck reaction. Reacting conditions: iodobenzene (1.0 mmol), styrene (1.1 mmol), potassium carbonate (2.0 mmol), Pd(II)@75% BPy COF (5 mg, containing slightly less than 0.01 mmol of Pd element), *N*,*N*-dimethylformamide (5 mL), 105 °C, 5 h, N₂ atmosphere. The conversion was monitored by GC using hexadecane as internal standard. The reaction was completed in 5 h. Inset: plot of log of the remaining iodobenzene concentration *versus* time which exhibited a first-order rate constant of *k* = 0.542 ± 0.034 h⁻¹.

rate constant of $k = 0.542 \pm 0.034 \text{ h}^{-1}$ when Pd(II)@75% BPy COFs was used as catalyst with iodobenzene as the substrate (Fig. 9). The good catalytic properties of the COFs prepared in the current study can be attributed to their higher Pd loadings (14.3-18.7 wt%) and the larger surface areas of the catalyst carriers (283-982 m²/g) compared to those reported in the literature [44]. The Pd(II)@75% BPy COF afforded the best catalytic performance of the four candidates tested, and was used further to evaluate its recyclability. Superior catalytic activity was maintained (>90% isolated yield) by this catalyst for up to four cycles (Fig. 10(a)). The crystalline structure of the scaffold of the COF was also found to be well preserved after each cycle (Fig. 10(b)), which highlighted the high stability of this catalyst in the catalytic environment. The heterogeneous nature of the catalyst was also confirmed using a leaching test. In a typical procedure, the supernatant was isolated after 1 cycle of the catalytic experiment and mixed with freshly pre-



Fig. 10. (a) Recyclability test of the Pd(II)@75% BPy COF catalyst for the Heck reaction. (b) PXRD patterns of the Pd(II)@75% BPy COF before and after the recycling test. Iodobenzene was selected as the model substrate for this reaction. All other reaction conditions see Table 1.

pared substrates for a new round of the reaction. It is found that very little conversion was obtained under these conditions. ICP-OES measurements also confirmed that no Pd element was being lost from the COFs after the reaction. On the basis of these results, it is likely that other reactions can also be catalyzed. These experiments will promote the application of COFs as catalysts.

4. Conclusions

We synthesized a series of 2D X% BPy COFs (X = 25, 50, 75, 100) containing two different nitrogen ligands (imine and bipyridine groups) as a support for the immobilization of Pd(OAc)₂. The total nitrogen content can be tuned from 6.8 to 10.3 wt% by varying the feed ratio of 2,2'-BPyDCA. Both bipyridine and imine groups behaved in a similar manner except for the binding location: imine groups favored binding in the space between adjacent COFs layers and bipyridine groups favored binding in the pores of the COFs. The Pd loading was determined by both the ligand content and surface area of the COFs, and could be varied between 14.3 and 18.7 wt%. Due to the high surface area and high Pd loading, the Pd(II)@X% BPy COFs exhibited outstanding catalytic efficiency in the Heck reaction. Pd(II)@75% BPy COF was the best catalyst of the four and its good recyclability and stability were also confirmed. These results offer a unique opportunity for the tuning of the structural parameters of COF-based heterogeneous catalysts.

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Graphical Abstract

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Nitrogen ligands in two-dimensional covalent organic frameworks for metal catalysis Jianqiang Zhang, Yongsheng Peng, Wenguang Leng *, Yanan Gao, Feifei Xu, Jinling Chai *



Bipyridine ligands and imine groups were both introduced into two-dimensional covalent organic frameworks (COFs) to dock with palladium(II) acetate and the metal loaded COFs exhibited good catalytic performance towards Heck reaction.

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