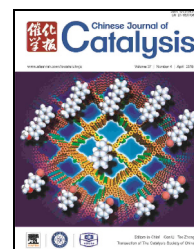


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## Article

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

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## 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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## 1. Introduction

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  $\pi$ - $\pi$  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 ( $\text{Pd}(\text{OAc})_2$ ), but the loading position of the  $\text{Pd}(\text{OAc})_2$  can be varied. The imine ligand favors binding  $\text{Pd}(\text{OAc})_2$  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,  $\text{Pd}(\text{OAc})_2$ , 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, di-

methylacetamide, 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(4-formylphenyl) 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 mesitylene/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  $(\text{C}_{67}\text{H}_{41}\text{N}_5)_n$ : 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  $(\text{C}_{66}\text{H}_{40}\text{N}_6)_n$ : 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  $(\text{C}_{65}\text{H}_{39}\text{N}_7)_n$ : 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  $(\text{C}_{64}\text{H}_{38}\text{N}_8)_n$ : 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.  $\text{Pd}(\text{OAc})_2$  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  $\text{Pd}(\text{OAc})_2$  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  $\text{Pd}(\text{OAc})_2$  and then dried at 120 °C under vacuum for 12 h to give Pd(II)@X% BPy COFs.

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