



# La-Metal-Organic Framework incorporating Fe<sub>3</sub>O<sub>4</sub> nanoparticles, post-synthetically modified with Schiff base and Pd. A highly active, magnetically recoverable, recyclable catalyst for C–C cross-couplings at low Pd loadings

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## ABSTRACT

Unprecedented post-synthetic modification (PSM) applied on a new La-MOF containing Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs), via Schiff base build-up (with pyridine-2-carboxaldehyde) and PdCl<sub>2</sub> coordination, proved to be an advantageous strategy to produce a superior heterogeneous catalyst for Suzuki-Miyaura C–C bond formation. The Fe<sub>3</sub>O<sub>4</sub>@La-MOF-Schiff base-Pd ensemble (characterized by PXRD, EDS, TEM, HAADF-STEM, VSM, TGA) showed very active, quite stable, magnetically recoverable and reusable in coupling of bromo- or iodoaryls with arylboronic acids, affording practically quantitative yields of biaryls (>99%) and high TONs and TOFs. The catalyst has been recycled up to 12 times without significant loss of the catalytic activity. A synergistic cooperativity between Pd and the oxophilic La nodes, through the organic linker, is responsible for enhancing the catalytic activity and stability.

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## 1. Introduction

As a new type of highly tailorable microporous materials, metal-organic frameworks (MOFs) are at the core of a variety of specific applications such as catalysis [1], gas storage [2], drug delivery [3a], sensors [3b] or diversified multifunctional materials [4]. In particular, MOFs have played a key role in heterogeneous catalysis as catalyst templates due to their high surface area, adjustable pore size, robustness, controllable distribution of the catalytically active sites, and increased activity and chemoselectivity [1,5]. Furthermore, post-synthetic modification (PSM) of MOFs has emerged as an important tool for introducing a wide range of functional groups into the complex MOF superstructures extending thus their use in catalysis according to current needs [6–8]. Presently, there are two PSM strategies for MOF functionalization. In the first, the newly introduced functions are connected to backbones of the MOFs by covalent, coordination or covalent-coordination modification [9,10]. For instance, amine groups on

MOFs, as target motifs, are frequently reacted with anhydrides [11,12] and aldehydes [13–15] via PSM to create multidentate coordination sites. The latter can further coordinatively bind metal ions, catalytically active, such as Pd (II), in view of efficient application in C–C cross couplings. The second method is to load nanoparticles, such as Au, Pt, Ni and Cu, in the void spaces of MOFs by the method of impregnation in metal salt solutions and reduction, then use the resulting modified MOFs as catalysts in well-defined reactions [16a]. However, a method implying the two above mentioned strategies for tailoring La-MOFs, which might further widen the perspectives of valorising these unique materials, has not been previously [16b] reported.

Palladium-catalyzed cross-couplings, conducted in homogeneous and heterogeneous phase, have been extensively applied in synthetic chemistry [17–21]. Among these, Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids represents an efficient way for forming carbon-carbon bonds, particularly for synthesis of biaryls as building blocks of pharmaceutical products [17]. In spite of this progress, isolation of homogenous catalysts from reaction mixtures is sometimes quite difficult and metal leaching is problematic leading to highly toxic palladium (II) residues [21a]. Although development of heterogeneous

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catalytic systems made it possible to isolate and recycle the recovered catalysts, some Pd leaching and cumbersome processes such as filtration and clogging still remain current issues that affect the reuse of conventional heterogeneous catalysts, especially when solid inorganic bases are employed. To meet these challenges, catalysts supported on magnetic nanoparticles (MNPs) offered a convenient use circumventing separation by centrifugation or tedious filtration, the catalyst being instead recovered simply by applying an external magnet [22]. Thus, Zhang and coworkers [23a] synthesized a palladium-2,2-bipyridine complex supported on  $\text{Fe}_3\text{O}_4$  nanoparticles and valorised it in Suzuki-Miyaura couplings. This catalyst could be easily separated magnetically. More recently, Astruc and coworkers [23b] took advantage of magnetically recoverable “click” PEGylated  $\gamma\text{-Fe}_2\text{O}_3\text{-Pd}$  nanoparticle catalysts in the Suzuki-Miyaura, Sonogashira, and Heck reactions, demonstrating intervention of strong positive dendritic effects on catalyst loading, catalytic activity, and recyclability. Also, superparamagnetic polymer composite microspheres ( $\text{Fe}_3\text{O}_4/\text{polymer}$ ), used to support palladium nanoparticles, provided high reactivity in Suzuki coupling reactions, while the catalyst could be easily recovered and reused for five times [23c]. Further notable applications of Pd on magnetic supports as catalysts in C–C bond formation have also been reported [23d,23e].

Prompted by these developments and continuing our research program on Pd-catalyzed cross-coupling reactions [18b,19b,19c], we have designed a highly efficient  $\text{Fe}_3\text{O}_4$  nanoparticle-supporting catalyst, synthesized via a PSM strategy operated on a La-MOF  $[\text{La}(\text{abdc})(\text{Habd})\cdot 9\text{H}_2\text{O}]_n$  ( $\text{abdc}$  = 2-amino-benzene-1,4-dicarboxylate), herein reported for the first time (Scheme 1). The significant robustness and fine porosity of this La-MOF, provided by the oxophilic La nodes and dicarboxylic organic linker, coupled with adequate stability to solvents and chemical reagents, were good reasons for choosing it as substrate for PSM [24–26]. Besides, our synthesis protocol is very simple so that this new catalyst can be made available on a large scale.

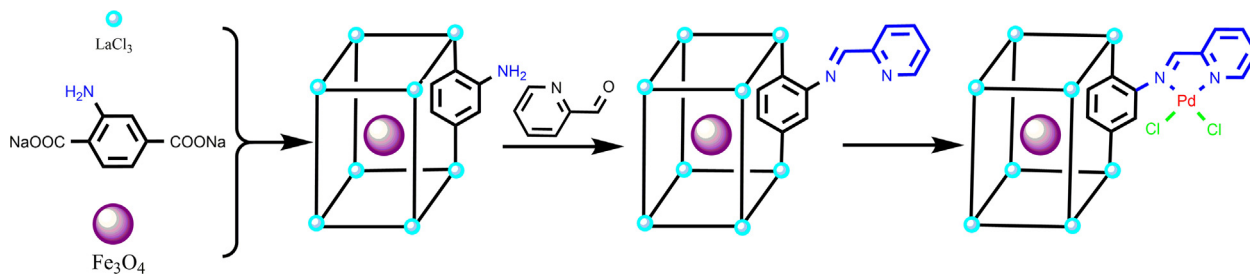
## 2. Experimental

### 2.1. Catalyst preparation

All starting materials and solvents were obtained and used without further purification from commercial suppliers.

#### 2.1.1. Synthesis of disodium 2-amino-benzene-1,4-dicarboxylate

Two equivalents of sodium hydroxide were added to a suspension of 2-amino-benzene-1,4-dicarboxylic acid ( $\text{H}_2\text{abdc}$ ) in distilled water and the mixture stirred until all components were fully dissolved. After adjusting the pH of the solution to 6 and heating it carefully in air to dryness, a pale yellow powder of disodium 2-aminoterephthalate was collected.



Scheme 1. Synthesis route of  $\text{Fe}_3\text{O}_4@$ La-MOF-Schiff base-Pd.

#### 2.1.2. Synthesis of magnetic $\text{Fe}_3\text{O}_4$ nanoparticles

$\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (2.7 g) and  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  (2.7 g) were added to distilled water (60 mL) and stirred until all the components were dissolved. A brown precipitate was generated by adding the right amount of  $\text{NH}_3\cdot \text{H}_2\text{O}$  (28%), under mechanical stirring. After adjusting the pH to 10, the solution was heated at  $80^\circ\text{C}$  for 0.5 h. The  $\text{Fe}_3\text{O}_4$  was collected and washed 3 times with distilled water and 3 times with ethanol. After drying, the obtained black  $\text{Fe}_3\text{O}_4$  powder (1.5987 g) was dispersed into ethanol at a concentration of 7 mg/mL.

#### 2.1.3. Synthesis of microcrystalline powder La-MOF

A microcrystalline powder of La-MOF was obtained by mixing in water stoichiometric amounts of lanthanide chloride and disodium 2-amino-benzene-1,4-dicarboxylate. Precipitation immediately occurred and the pale-yellow precipitate was filtered and dried in air.

#### 2.1.4. Synthesis of single crystal La-MOF

$\text{NaOH}$  (0.1 M) was added dropwise to 10 mL water solution of  $\text{H}_2\text{abdc}$  (0.018 g, 0.10 mmol) adjusting the pH value to 5–6, and the resulting solution was introduced into a test tube. A new solution of  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (0.044 g, 0.10 mmol) in 2-propanol (8 mL) was allowed to slowly diffuse into the above solution of  $\text{H}_2\text{abdc}$  through a buffering layer of 2-propanol and water (1:1). Colorless cubic crystals suitable for X-ray crystal analyses were obtained after four days (yield 20%), which are stable in air and insoluble in water and common organic solvents

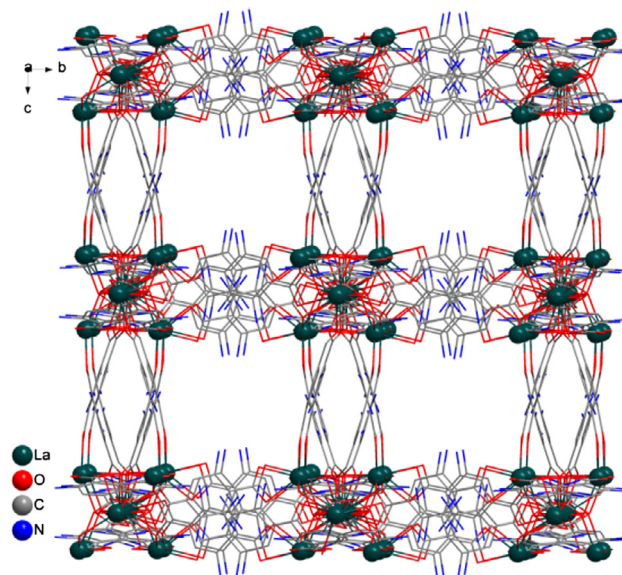


Fig. 1. The 3D structure of La-MOF highlighting the 4-nodal topology of the La-MOF subunit.

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