

High catalytic active palladium nanoparticles gradually discharged from multilayer films to promote Suzuki, Heck and Sonogashira cross coupling reactions



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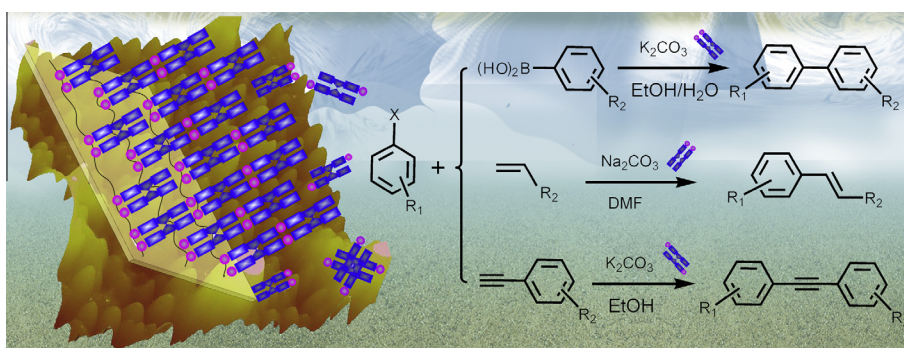
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HIGHLIGHTS

- The release amount of catalysts could be easily controlled by removing the film.
- High catalytic efficiency with extremely low Pd-loading down to 10^{-6} mol%.
- High stability in the air and free phosphorus ligands.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve the catalytic activity and reduce the dosage of noble metal catalysts has attracted much more attention for organic synthetic chemists. We facilely fabricated multilayer films of PEI-(PdCl₂/1)_n through layer-by-layer (LbL) self-assembly method (PEI = polyethylenimine, 1 = 2,2',7,7'-tetra(4-pyridyl)-9,9'-spirobifluorene, psf). UV-vis spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to monitor the growth of multilayer films. X-ray photoelectron spectroscopy (XPS) proved the palladium and ligand 1 were deposited on the film. The PEI-(PdCl₂/1)_n multilayer films were used as the cisterns of catalysts to gradually discharge high active catalytic moieties in the Suzuki–Miyaura, Heck and Sonogashira cross-coupling reactions. The Pd-loading was as low as 12.1×10^{-6} mol% measured by inductively coupled plasma OES spectrometer (ICP), and gave high yields in the typical reactions of bromobenzenes with phenylboronic acids. The LbL catalyst featured the simplicity of fabrication, high efficiency, reusability, convenient control and no sensitive to air in the reactions.

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1. Introduction

The carbon–carbon cross-coupling reactions for forming biaryl compounds have become one of the most powerful and convenient synthetic protocols in organic chemistry, due to the stability of the

starting materials, tolerance of functional groups and compatibility to a range of solvents [1–3]. There are two critical questions in modern organic syntheses of carbon–carbon coupling reactions: (1) how to minimize the catalyst cost as low as possible [4]; (2) how to improve the efficiency and reusability of the catalyst [5]. In the past decades, many efforts have been made to develop high efficient catalytic systems for the coupling reactions including

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heterogeneous and/or homogeneous catalysts. For example, palladium–phosphine complexes and N-heterocyclic carbenes have received great attention due to the high catalytic activity in recent decades [6–10]. However, a series of drawbacks have been present such as the expensiveness of ligands, air-sensitivity and larger loading [11,12]. What's more, how to efficiently recycling catalysts still remain great challenges in industrial applications now. In order to overcome the disadvantages above, the supported Pd-catalysts have been successfully designed by immobilizing the Pd-catalysts onto organic and inorganic supporters, such as mesoporous silica [13], proteins [12], carbon nanotubes [14], partially reduced graphene oxide nanosheets [15], NaY zeolites [16], magnetic nanoparticles [17], polymeric microspheres, microcapsules and resins [18–22]. Although most of them exhibited high thermal stability and excellent catalytic activity, the others showed less efficiency compared with homogeneous catalysts. It was worth noting that the good conversion was usually obtained at high temperatures above 100 °C and relatively high catalyst loading (3–5% based on organic media) [12,23].

Considering the advantages and the weakness of homogeneous and heterogeneous catalysis, we designed a new homogenized quartz substrate-supported Pd/organic ligand catalyst. The key step is to choose appropriate ligands and methods to assemble the compounds onto the substrates. Recently, rigid organic ligands with conjugated pyridyl groups Pd/*trans*-[Pt(PPh₃)₂(C≡CPy)₂] and Pd/[Pt₂(dppm)₂(C≡CPy)₂] as the supports to assemble multilayer films were reported [24,25]. Inspired by this, the ligand **1** was prepared in our laboratory instead of the noble metal complexes and used for the formation of the PEI-(PdCl₂/**1**)_n multilayer films based on the layer-by-layer (LbL) technology. The method benefited from lower loading, which developed its application in the parallel syntheses of libraries requiring different type of transformation.

Herein, a new π -conjugated ligand of 2,2',7,7'-tetra(4-pyridyl)-9,9'-spirobifluorene (psf, **1**, Scheme 1) as a co-catalyst was synthesized and characterized by NMR, IR, UV–vis, MS, and fluorescent spectra (Fig. S1–6 in Supplementary Materials). The fabrication of PEI-(PdCl₂/**1**)_n films and their applications as the catalysts in Suzuki, Heck and Sonogashira reactions between boronic acids/alkene/alkyne and aryl halides were carried out. Our strategy was to attach a PEI layer on the quartz substrate, and then the substrate was dipped in PdCl₂ solution, allowing the Pd²⁺ and PEI to form a PEI-Pd²⁺ thin film. Afterward, the substrate was immersed in the ligand solution, and the ligand would combine with Pd(II) ions by the coordination bond to form another film. The multilayer films were obtained by repeating the steps above, which were used as the catalyst reservoir capable of discharge high active Pd-catalysts to promote the coupling reactions [24–27]. All the Suzuki, Heck and Sonogashira reactions occurred under atmospheric condition without any specific protection and no phase-transfer agents added.

2. Experimental

2.1. Materials and methods

Poly(ethylenimine)(PEI, MW = 60,000, 10 wt% aqueous solution) was purchased from Aldrich Chemical Co. All reagents were of analytical grade and used directly without further purification. Solutions were prepared with deionized water (Milli-Q,

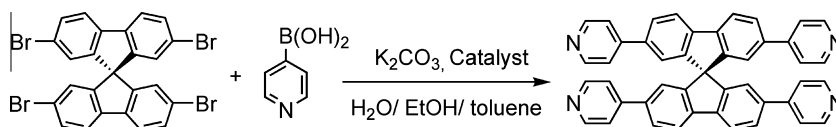
18.2 M Ω cm). Infra-red spectra were recorded on a Nicolet Avatar FTIR spectrophotometer in the range 4000–400 cm⁻¹. Gas chromatography-mass spectrometry (GC–MS) was performed on a 430 GC (Varian, USA). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained in CDCl₃ solutions using a Bruker AVANCE 400 spectrometer. Fluorescence spectra were collected by the FLS920 fluorescence spectrometer. UV–vis spectra were recorded on a quartz slide with a Lambda35 spectrophotometer (Perkin-Elmer, USA). High-resolution XPS was collected at a takeoff angle of 45° using PHI Quantum 2000 SCANNING ESCA microprobe (Physical Electronics, USA) with an Al α X-ray line (1486.6 eV). All AFM images were taken on single crystal silicon slides using a Veeco Multimode NS3A-02NanoscopeIII atomic force microscope with silicon tips. Height images of the films were recorded using tapping-mode AFM. Analysis of Pd content was measured by an inductively coupled plasma OES spectrometer (ICP, Ultima2, France). SEM images were taken with SU-70 field-emission scanning electron microscope. TEM images were carried out by Tecnai G2 F20 S-TWIN. Energy dispersive X-ray spectrometer (EDS) was carried out on a Carl Zeiss model Ultra 55 microscope.

2.2. Synthesis of 2,2',7,7'-tetra(4-pyridyl)-9,9'-spirobifluorene (**1**)

The preparing procedure of **1**: 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (1.5 mmol), pyridine-4-boronic acid (9.0 mmol), K₂CO₃ (30 mmol), and Pd(PPh₃)₄ (0.15 mmol) were dissolved in toluene/EtOH/H₂O [28], and the reaction mixture was heated to 90 °C. After refluxing for 48 h under N₂, the mixture was cooled to the room temperature, and then extracted with CH₂Cl₂ for three times. The organic phase was dried with anhydrous MgSO₄, and concentrated by evaporation under reduced pressure. The obtained samples were purified by column chromatography, yield 75%. For **1**, element anal. Calcd (%): C, 86.54; H, 4.49; N, 8.97. Found(%): C, 86.53; H, 4.50; N, 8.97. ¹H NMR (CDCl₃, 400 MHz): 8.530–8.514 (d, 8H, –C₅H₄N), 8.052–8.072 (d, 4H, –C₆H₃), 7.750–7.774 (d, 4H, –C₆H₃), 7.356–7.371 (d, 8H, –C₅H₄N), 7.055–7.058 ppm (d, 4H, –C₆H₃); ¹³C NMR (CDCl₃, 100 MHz): δ = 150.0(C), 149.5(C), 147.8(C), 142.0(C), 138.5(C), 127.6(CH), 122.6(CH), 121.5(CH), 121.4(CH), 66.15(Cspiro) ppm. HR-MS (ESI): *m/z* calcd for C₄₅H₂₈N₄: 624.4; found 625.4 (M + H⁺).

2.3. Fabrication of PEI-(PdCl₂/**1**)_n multilayer films

The quartz slides (25 × 12 × 1.0 mm) were cleaned with a mixture solution of H₂SO₄/H₂O₂ (7:3, V/V) (**Caution!** Piranha solution is extremely corrosive) at 80 °C for 30 min, and thoroughly rinsed with distilled water. Further purification was carried out by immersion in a H₂O/H₂O₂/NH₄OH (5:1:1) (V/V/V) solution at 70 °C for 30 min. Then clean slides were immersed in PEI solution (10 wt%, 20 mL) for 20 min. After that the pre-coated PEI slides were alternately immersed in aqueous solution of PdCl₂ (5.0 mM) and ethanol solution of **1** (5.0 mM) for 30 min. Substrates were washed with deionized water and dried with a nitrogen stream after each immersion. PEI-(PdCl₂/**1**)_n films were prepared by repeating the above procedure [24–27], as shown in Scheme 2.



Scheme 1. Synthesis schematic diagram of the **1** ligand.

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