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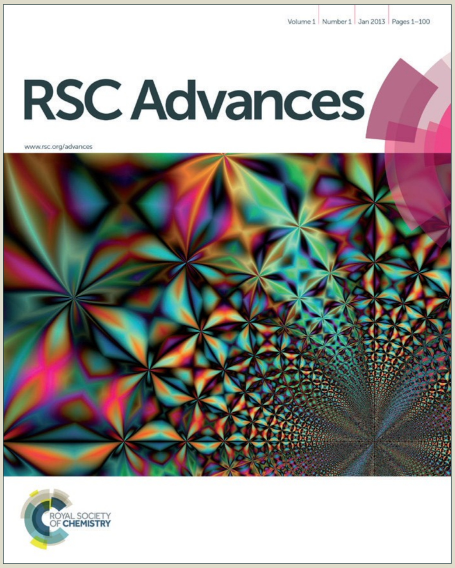

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Bipyridyl Palladium Embedded Porous Organic Polymer as Highly Efficient and Reusable Heterogeneous Catalyst for Suzuki-Miyaura Coupling Reaction

Chang-An Wang*, Yin-Feng Han, Yan-Wei Li, Kun Nie, Xue-Li Cheng, and Jian-Ping Zhang

Abstract: Two robust porous organic polymers embedded with bipyridyl ligand (Bpy-POP) were obtained via a bottom-up strategy. After a simple post-treatment, a Pd(II)-containing POP (Bpy-Pd-POP) was used as highly efficient and reusable heterogeneous catalyst for the Suzuki-Miyaura coupling reaction. It could be reused at least 15 times without significant loss of the catalytic activity (97-99% yield).

Chelating ligands containing pyridyl moieties are extensively used ligand frameworks in coordination chemistry[1] and homogeneous catalysis[2]. As one of the most important chelating ligands, the bipyridines has offered an interesting alternative in developing catalytic systems for organic synthesis due to its robust redox stability, coordinating ability with a wide range of metal ions and ease of functionalization.[2a-b,2e] However, many noble metals used in homogeneous catalysis are quite expensive and it is difficult to separate the ligand-metal catalysts from the reaction system, which restricted their practical application on a large scale. Accordingly, immobilization of homogeneous catalysts using a solid support provide an interesting approach to solve these vital problems.[3]

In this context, Porous organic Polymers (POPs),[4] due to their large surface area, low skeletal density and high chemical stability, have attracted particular attention as a new class of porous materials for various potential applications.[5-9] In particular, POPs have provided a highly tunable platform for designing heterogeneous catalysts via the embeddedness of rigid catalytic active monomers into the frameworks.[10] Importantly, the bipyridine ligand coordinated with metal ions embedded POPs framework was shown high catalytic activity for heterogeneous catalysis. For example, Lin and co-workers developed the synthesis of phosphorescent $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$-incorporating porous cross-linked polymers for efficient photocatalysis.[11] Cooper and co-workers elaborated the synthesis of a series of the bipyridine metal-functionalized conjugated microporous polymers as an efficient heterogeneous catalyst for reductive amination.[12] However, to the best of our knowledge, the recyclable and reusable (<5 times) of these bipyridine metal-functionalized POPs are not satisfactory. Therefore, towards the practical applications of POP catalysts, the following criteria should be considered: i) The synthesis of POP catalysts should be concise and based on inexpensive chemicals; ii) The POP catalysts should be robust and has high activity and selectivity; iii) The POP catalysts should possess persistent recycling and reusing.

With these considerations in mind, herein, we report the synthesis of two robust porous organic polymers embedded with bipyridyl ligand (**Bpy-POP**) via a bottom-up strategy. After being post-modified with palladium ions, these polymers (**Bpy-Pd-POP**, Scheme 1) could be utilized as highly efficient and recyclable heterogeneous catalysts for carbon-carbon coupling reaction. Inspired by the pioneering work of Cooper and co-workers, where the surface area and the pore size of CMPs could be tuned by varying the molecular length of the rigid building blocks (alkynes).[13] Accordingly, we could synthesize two robust bipyridyl-functionalized POPs with tunable surface areas and pore size distributions, and preliminary investigate the influence of the properties on the catalytic activity.

The polymer networks were constructed by palladium-catalyzed Songashira-Hagihara cross-coupling reaction of 4,4'-dibromo-2,2'-bipyridine (**1**) as the functional building blocks with tetra(4-ethynylphenyl)methane (**2**) or 1,3,5-triethynylbenzene (**3**) as the structural building blocks(see the Supporting Information for experimental details). The general synthetic routes for the **Bpy-POP** networks are shown in scheme 1. Both of the obtained polymers **Bpy-POP-1** and **Bpy-POP-2** are a dark brown powder, and are insoluble in all of the solvents tested. The polymer is thermally stable up to 400 °C under nitrogen atmosphere (TGA result for **Bpy-POP** shown in Figure S1 and S2 in the Supporting Information). Powder X-ray diffraction measurements indicated that the **Bpy-POP** network is amorphous in nature (Figure S3, SI).

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[a] *College of Chemistry and Chemical Engineering, Taishan University, Tai'an Shandong 271000 (P. R. China)
E-mail: wangcha_chem@163.com.*

† Footnotes relating to the title and/or authors should appear here.

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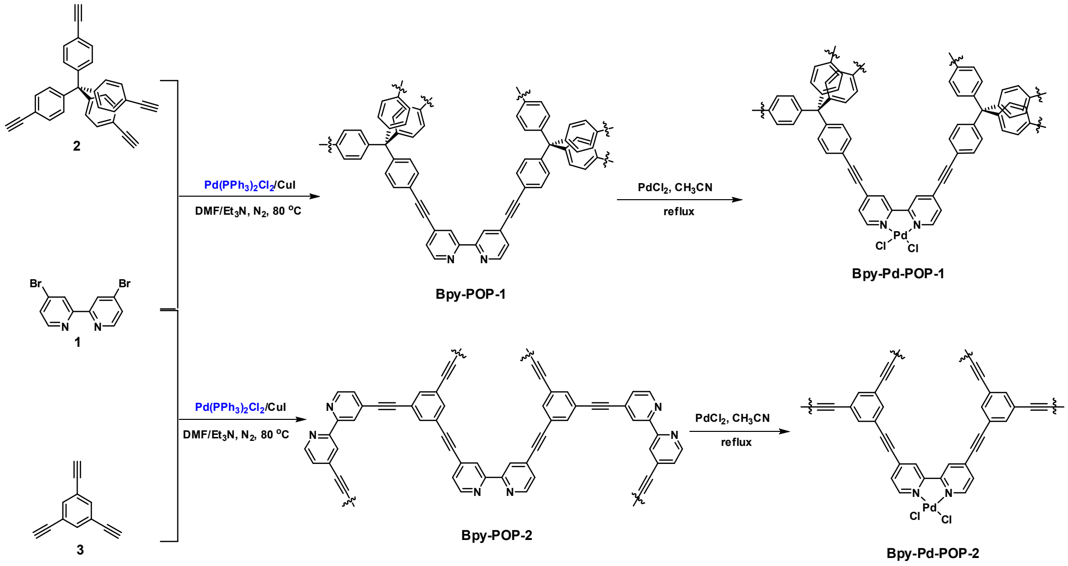

Scheme 1. Synthesis of bipyridyl palladium catalyst-embedded porous organic polymers

The permanent porosity of **Bpy-POP** was investigated by nitrogen sorption measurements at 77 K, and the obtained results are listed in Table S1. The application of the Brunauer-Emmett-Teller (BET) modal resulted in the surface areas of 506 and 443 m^2g^{-1} for **Bpy-POP-1** (Figure S4, SI) and **Bpy-POP-2** (Figure S5, SI), respectively. By comparing **Bpy-POP-1** (monomer 2) and **Bpy-POP-2** (monomer 3), we found that the polymer networks with long-lengthed building block had a higher BET surface area (506 m^2g^{-1} *vs* 443 m^2g^{-1}). In Figure 1(a) and (b) are shown the N_2 volume adsorbed, V_{ads}, *vs.* relative pressure P/P_o, for **Bpy-POP-1** and **Bpy-POP-2**. According to the IUPAC classification, **POP-1** displays a Type-IV gas sorption isotherm with H2 hysteresis loops, indicating that this polymer consist of mesoporous and **POP-2** displays a Type-I gas sorption isotherm reflecting the presence of abundant micropores structure. From t-plot analysis, the **Bpy-POP-1** ploymer displays both a microporous contribution of 206 m^2g^{-1} (40.7%) and a mesoporous contribution of 300 m^2g^{-1} (59.3%). As calculated by non-local density functional theory (NLDFT), the pore size distribution (PSD) of **Bpy-POP-1** and **Bpy-POP-2** mainly distributed around 0.7 and 1.3 nm, respectively (Figure 1(c) and (d)). However, the broad PSD curves of **POP-1** also suggest the co-existence of micro- and mesopores in the polymer networks. Specifically, the constructed mesopores greatly facilitate the mass transport process. After being post-modified with $PdCl_2$, the BET surface area of **Bpy-POP-1** decreases to 394 m^2g^{-1} due to the $PdCl_2$ hanging in the pore volume.

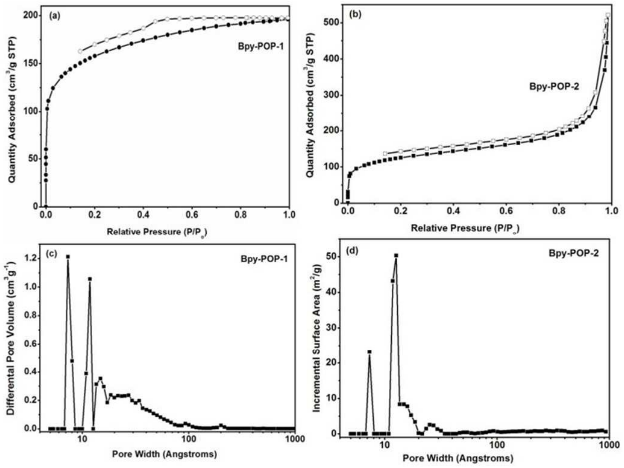

Figure 1. Nitrogen sorption isotherm of **Bpy-POP-1** (a) and **Bpy-POP-2** (b). Pore size distribution (PSD) for **Bpy-POP-1** (c) **and Bpy-POP-2** (d), calculated with non-local density functional theory (NLDFT).

The chemical composition of **Bpy-POP** were characterized by solid-state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy. Figure 2 shows the ^{13}C CP/MAS NMR spectra recorded for **Bpy-POP-1**. The signals at $\delta = 121$, 149 and 155 ppm confirmed that the bipyridyl monomer skeleton has well been embedded into the polymer networks, while the peak at approximately 88 and 93 ppm represent the alkynyl groups in the polymers. The peak at about 65, 131 and 149 ppm also confirm that the tetra(4-ethynylphenyl)methane skeleton has been successful embedded into the frameworks. Additionally, elemental analysis of **Bpy-POP** polymer identified the content of nitrogen (6.59% and 8.00%), based on

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which the molar loading of bipyridyl ligand moieties could be calculated. All of the results proved the successful synthesis of the polymer networks.

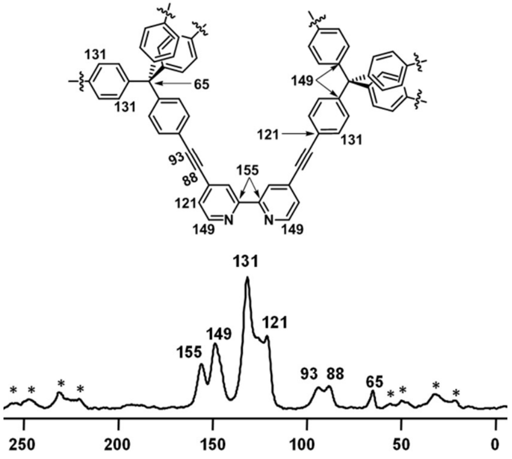


Figure 2. Solid-state ^{13}C CP/MAS NMR spectra for **Bpy-POP-1**. The assignments for the ^{13}C MAS NMR signals are indicated (top). ^{13}C CP/MAS NMR spectra for **Bpy-POP-2** are shown in Figure S6.

Next, through a simple post-treatment of **Bpy-POP** with palladium chloride (Scheme 1), the porous organic catalyst **Bpy-Pd-POP** was facilely prepared (see SI for details). We then performed X-ray photoelectron spectroscopy (XPS) measurements to investigate the incorporation of palladium within **Bpy-Pd-POP-1.** As shown in Figure 3 (red), the binding energy (BE) at 336.88 eV correspond to $Pd_{3d5/2}$ orbitsal in **Bpy-Pd-POP-1**, which indicated that the Pd species is present in +2 state.[14] The BE of 336.88 eV for the Pd species in **Bpy-Pd-POP-1** shifted negatively 0.75 eV in comparison with that of 337.63 eV for free $PdCl_2$ (Figure 3, black), which indicates the strong coordination of $PdCl_2$ with the bipyridyl ligand of **Bpy-POP-1** polymer. In addition, the slight difference in the FT-IR spectra of **Bpy-POP** and **Bpy-Pd-POP** also indicates that the coordinated palladium chloride in the polymer (Figure S7 and S8, SI).

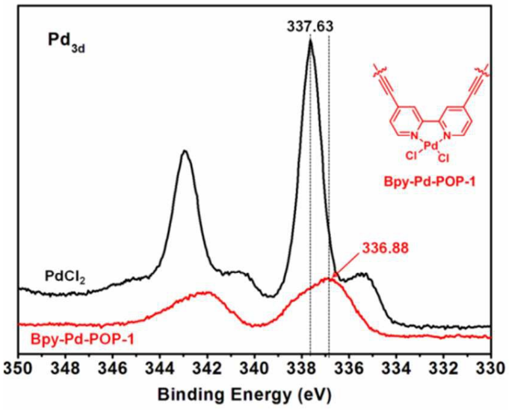
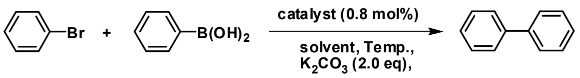


Figure 3. XPS spectra for free $PdCl_2$ (black) and **Bpy-Pd-POP-1** (red).

The Suzuki-Miyaura coupling reaction is one of the most versatile methods for the facile formation of C-C bonds, which has attracted extensive attention in recent years.[15] To evaluate the catalytic activity of **Bpy-Pd-POP** as a robust heterogeneous catalyst, we accordingly chose the Suzuki-Miyaura coupling reaction of phenylboronic acid with bromobenzene as a model reaction (Table 1). Using **Bpy-Pd-POP-1** polymer as the catalyst, the reaction occurred smoothly in EtOH at 80 °C to give the desired product with high yield (Table 1, entry 1). Further investigation on the effect of reaction media was conducted (Table 1, entries 2-6) and mixture solvent of EtOH and H_2O with a ratio of 1/1 gave the best result (Table 1, entry 6, 99% yield). The effect of temperature on this reaction was also examined (Table 1, entries 7-8), when the temperature was lower to 60 °C, the reaction proceeded much slower in EtOH/H_2O (1:1, v/v) and a product yield of 95% could be achieved in more than 2 h (Table 1, entry 7). We hoped to investigate the influence of the properties on the catalytic activity, unfortunately, the **Bpy-Pd-POP-2** polymer showed similar reactivity to **Bpy-Pd-POP-1** under this system (Table 1, entry 9). Finally, the optimized condition for the Suzuki-Miyaura coupling reaction was chosen as: EtOH/H_2O (1:1, v/v) as the co-solvent, 0.8 mol% **Bpy-Pd-POP-1** as the heterogeneous catalyst, in the presence of potassium carbonate, and at 80 °C.

Table 1. Screening conditions for the Suzuki-Miyaura coupling reaction.[a]



Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	TON[c]
1	**Bpy-Pd-POP-1**	EtOH	80	1	95	119
2	**Bpy-Pd-POP-1**	H_2O	80	1	85	106
3	**Bpy-Pd-POP-1**	Toluene	80	3	60	75
4	**Bpy-Pd-POP-1**	CH_2Cl_2	80	3	52	65
5	**Bpy-Pd-POP-1**	DMF	80	3	60	75
6	**Bpy-Pd-POP-1**	EtOH/H_2O (1:1)	80	0.5	99	124
7	**Bpy-Pd-POP-1**	EtOH/H_2O (1:1)	60	2	95	119
8	**Bpy-Pd-POP-1**	EtOH/H_2O (1:1)	100	0.5	99	124
9	**Bpy-Pd-POP-2**	EtOH/H_2O (1:1)	80	0.5	98	123
10	------	EtOH/H_2O (1:1)	80	3	n.d.	0

[a] General condition: phenylboronic acid (0.5 mmol), bromobenzene (1.0 mmol), K_2CO_3 (1.0 mmol), and catalyst (0.8 mol%), solvent (1.0 mL), temperature. [b] Isolated yield after silica gel column chromatography. [c] TON =(moles of product)/(moles of metal in the catalyst), unless otherwise noted.

Having established the optimized reaction conditions, we tested a variety of substituted aryl halides to probe the versatility of our catalytic system (Table 2). As shown in Table 2, good to excellent isolated yields (93-99%) were obtained for all of the Suzuki-Miyaura coupling reaction of a variety of

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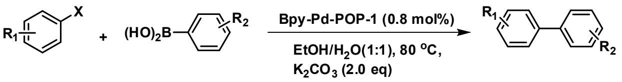
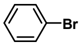
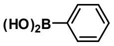
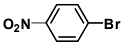
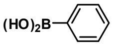
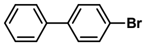
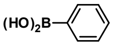
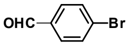
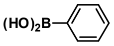
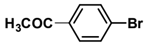
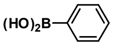
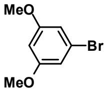
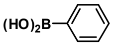
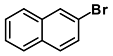
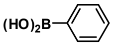
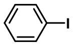
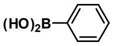
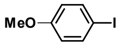
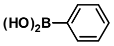
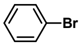
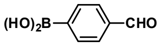
bromo and iodo derivatives with phenyboronic acid catalyzed by the **Bpy-Pd-POP-1** catalyst (Table 2, entries 1-9). For aryl iodides, the coupling reactions were rapidly completed within 0.5 h, giving the corresponding products with high yield (Table 2, entries 8-9). The phenyboronic acid substrate with an electron-withdrawing substituent could also be converted into the corresponding adduct in high yield (Table 2, entry 10). These results identified that the **Bpy-Pd-POP-1** nanoporous polymer works as a highly efficient heterogeneous catalyst for the Suzuki-Miyaura coupling reaction.

Table 2. Investigating the substrate scope of the Suzuki-Miyaura coupling reaction catalyzed by Bpy-Pd-POP-1.[a]



Entry	Ar-X	Ar-B(OH)$_2$	Time (h)	Yield (%) [b]
1			0.5	99
2			1.5	93
3			7	99
4			2	98
5			2	98
6			1	99
7			3	99
8			0.5	99
9			0.5	94
10			2	99

[a] General condition: phenylboronic acid (0.75 mmol), aryhalide (0.5 mmol), K_2CO_3 (1.0 mmol), and **Bpy-Pd-POP-1** (0.8 mol%), EtOH/H_2O (1.0 mL), 80 °C. [b] Isolated yield after silica gel column chromatography.

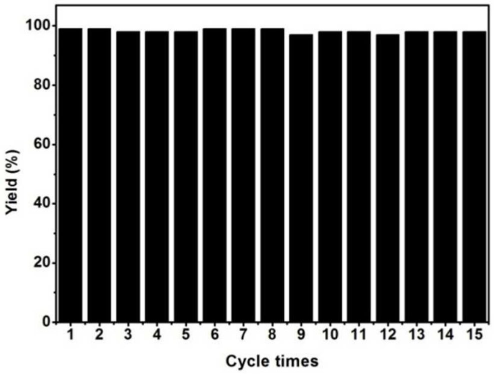


Figure 4. Recycling experiment of **Bpy-Pd-POP-1** for the Suzuki-Miyaura coupling reaction of bromobenzene and phenylboronic acid.

Next, we examined the recyclability of this porous organic catalyst **Bpy-Pd-POP-1** (see Supporting Information, Table S2). The recycling experiment was performed by using a simple centrifugation method to recover the heterogeneous catalyst. The recovered polymer was washed with EtOH and EtOAc to remove the residual product, and simple dried in vacuum overnight before reuse. As shown in Figure 4, Owing to the built-in character of the covalently linked catalytic sites in the polymer networks, the **Bpy-Pd-POP-1** nanoporous catalyst can be reused at least fifteen times without any significant loss of the catalytic activity (97-99% yield).[16] To determine that the reaction between bromobenzene and phenylboronic acid was indeed catalyzed by **Bpy-Pd-POP-1** instead of the dissolved homogeneous Pd species leached from the supports, the following strategy was adopted. When the phenylboronic acid conversion reached about 50%, the solid catalyst was removed from the hot reaction mixture and then the mother liquor was allowed to reaction another 2 h under the same conditions.[10f, 17] No significant change in conversion or yield could be observed. This study identified that $PdCl_2$ is strongly coordinated within **Bpy-POP** polymer and the active phase was not the dissolved Pd species leached from the polymer. In addition, XPS characterization of **Bpy-Pd-POP-1** after catalytic runs showed the well-retained state of Bpy-Pd(II) catalytic species (Figure S9, SI) and TEM images showed no Pd(0) nanoparticles were appeared in the frameworks of the recycled catalyst (Figure S10, SI).

To summarize, we have reported a powerful strategy to prepare Pd(II) organometallic catalyst immobilized on the bipyridyl ligand-functionalized porous organic polymer (**Bpy-POP**). Owing to the high BET surface area, covalently linked catalytic sites, wide opening and interconnected pores, the **Bpy-Pd-POP** displays high efficient activity and excellent recyclability for the Suzuki-Miyaura coupling reaction. The catalyst could be reused at least 15 times without significant loss of the catalytic activity (97-99% yield). We believe that **Bpy-Pd-POP** may act as a promising heterogeneous catalyst applicable to a variety of carbon-carbon coupling reactions, the topic of which is under further research in our laboratory.

Acknowledgements

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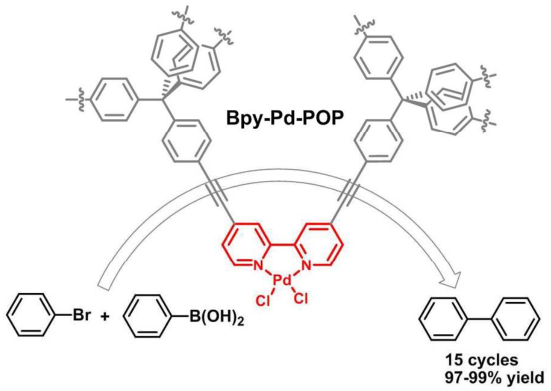

Bipyridyl-palladium catalyst embedded porous organic polymers (**Bpy-Pd-POP**) was synthesized and used as highly effective and reusable heterogeneous catalyst for the Suzuki-Miyaura coupling reaction. This porous organic catalyst could be reused at least 15 times without significant loss of the catalytic activity (97-99% yield).