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Pd-Metalated Conjugated Nanoporous Polycarbazoles for Additive-Free Cyanation of Aryl Halides: Boosting Catalytic Efficiency via Spatial Modulation

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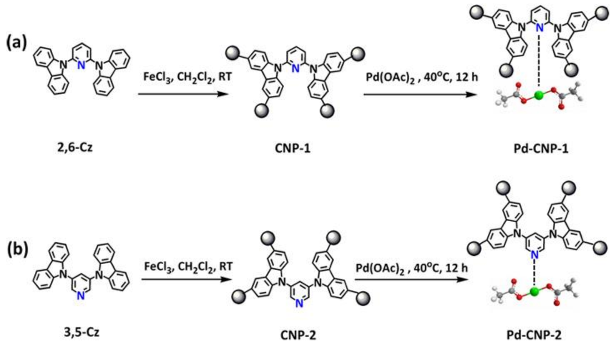
Abstract: A novel spatial-modulation approach was developed to fabricate a new heterogeneous Pd-metalated nanoporous polymer for efficient and ligand-free cyanation of aryl halides. The resulting catalyst displays high activity in the synthesis of benzonitriles, including high product yield, excellent stability and recycle, and broad scope functional group tolerance.

Benzonitriles, an integral part of dyes, pesticides, natural products and pharmaceuticals, are prevalent in organic chemistry owing to the versatile nature of the nitrile moiety, which can serve as an excellent synthetic handle to install a wide variety of functional groups such as amines, amides and ketones.[1] Transition-metal-catalyzed cyanation of aryl halides represents a common and powerful strategy for the construction of nitriles.[2] Of particular note are examples of Pd-catalyzed cyanation using $K_4[Fe(CN)_6]$ as nontoxic and inexpensive cyanide sources.[3] Nevertheless, most of these conventional homogenous systems involve the use of expensive additional ligands and suffer from poor recyclability, limiting their industrial application. Therefore, developing an efficient heterogeneous analogue is highly desired.

Conjugated nanoporous polymers (**CNP**s), formed by linking multidentate organic scaffolds through covalent bonds, have attracted tremendous attention in the context of heterogeneous catalysis,[4] due to the extent to which they can be synthetically tuned to enable molecular design of catalytic sites and access to diverse nano-pore regimes. Nevertheless, the use of **CNP**s that enable efficient cyanation of aryl halides towards the synthesis of benzonitriles, is rarely reported.

Herein, we report a novel spatial-modulation (**SM**) approach to generating Pd-metalated **CNP**s for this important chemical transformation. The key of our success lies in the use of rationally-designed polymeric backbones to create a favorable Lewis basic microenvironment within the nanoporous framework that encourages strong binding and stabilization of Pd (II), facilitating formation of the catalytically active species which can work with to initiate the cyanation. Under a heterogeneous, ligand-free condition, full conversion of aryl halides and excellent recyclability were successfully achieved for the resultant Pd-metalated **CNP** catalyst.



Scheme 1. Synthesis of (a) **Pd-CNP-1** and (b) **Pd-CNP-2**.

We designed and synthesized a model **CNP-1**, using a $FeCl_3$-catalyzed carbazole oxidation reaction (**Scheme 1a**).[5] We reasoned that the use of a pyridine-functionalized moiety as the building block would enable construction of a basic microenvironment for the cyanation,[3e] and at the same time afford electron rich active sites to strongly bind Pd (II) species in place of conventional expensive ligands.[3e] Through a facile impregnation approach, 1.3 wt.% Pd was loaded inside the Pd-metalated network (**Pd-CNP-1**) according to the Inductively coupled plasma (ICP) result (Table S1). The relevant Brunauer-Emmett-Teller (BET) surface area was determined to be 1070 m^2 g^{-1} (Table S1), with a Type I Nitrogen adsorption profile (Figure S1). The value is 247 m^2 g^{-1} lower than that of the non-metalated **CNP-1**. The marked hysteresis loop may be attributed to pore network effects.[6] The existence of the mesopores can be suggested from the pore size distribution curves (Figure S2).

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We initially focused the cyanation of 1,4-dibromobenzene (DBB) using $K_4[Fe(CN)_6]$ as the cyanide source to assess the activity of our Pd-metalated **CNP**-based catalyst. Unfortunately, negligible conversion of DBB to 1,4-dicyanobenzene (DCB) on **Pd-CNP-1** was observed under additive-free condition (4 %, entry 3, Table 1). We reasoned that Pd-loading at the sterically-hindered pyridinic binding sites may account for this poor catalytic performance. In this regard, we sought to improve the local environment of the catalytic Pd (II) species via a spatial modulation of the framework backbone, and therefore significantly enhancing the cyanation activity. A new building block, 3,5-di(9H-carbazol-9-yl)pyridine (**3,5-Cz**, **Scheme 1b**), was rationally synthesized in an effort to confirm our hypothesis. The resultant **CNP-2** exhibits a high BET surface area of 1538 m^2 g^{-1} (Figure S1). Due to the greater accessibility of the pyridine nitrogen, much higher Pd-loading (8.7 wt %, Table S1) can be introduced into **Pd-CNP-2**, commensurate with a significant reduction in BET surface area (865 m^2 g^{-1}). Furthermore, the existence of acetate-based moieties can be confirmed by the thermal gravimetric analysis (TGA, Figure S3). Nevertheless, this porosity remains sufficient for the facile transport of reactants to access the active sites inside the Pd-metalated network.

The significant differences in Pd-loading prompted us to pursue a better understanding of the spatial effect on the interaction between the Pd (II) source and rigid **CNP** frameworks. As such, we performed density functional theory (DFT) calculations to model the interaction between carbazolic-substituted pyridines (**2,6-Cz** and **3,5-Cz**) and $Pd(OAc)_2$, with results displayed in **Figure 1** (calculation details are provided in the supporting information).[5e] Importantly, the absolute value of the binding energy (|BE|) for **3,5-Cz**-$Pd(OAc)_2$ complex is 23.2 kcal mol^{-1}, four times larger than that of **2,6-Cz**-$Pd(OAc)_2$ (**Figure 1**), implying that **CNP-2** is more favourable for binding $Pd(OAc)_2$ than **CNP-1**. Accordingly, the spatial modulation of pyridinic sites play a crucial role in such high incorporation of Pd-containing sites.

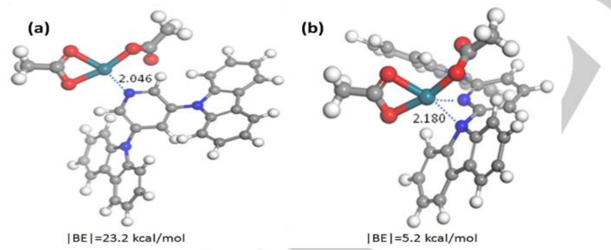
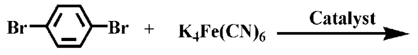


Figure 1. The complexes structures of **3,5-Cz**-$Pd(OAc)_2$ (a) and **2,6-Cz**-$Pd(OAc)_2$ (b). Color code: H, white; C, grey; N, blue; Pd, green; O, red.

The incorporated Pd-containing species were then studied by the powder x-ray diffraction (PXRD). No obvious peak can be observed from the PXRD pattern (Figure S4), indicating Pd is incorporated as a molecular complex. We further performed X-ray photoelectron spectroscopy (XPS) to obtain a deeper understanding of these sites (**Figure 2**). The Pd3d XPS spectra of **Pd-CNP-2** shows two deconvoluted peaks for Pd (Pd *3d5/2* peak at 338.3 eV and Pd *3d3/2* peak at 343.6 eV), confirming that the Pd(II) species are located on the surface of **Pd-CNP-2**.[7]

Table 1. Performances of different catalysts in cyanation of 1,4-dibromobenzene (DBB) with $K_4[Fe(CN)_6]$. [a]



Entry	Catalyst	t (h)	Yield (%) [f]	TON [g]
1	**CNP-1**	18	0	-
2	**CNP-2**	18	0	-
3[b]	**Pd-CNP-1**	18	4	65
4[c]	**Pd-CNP-2**	18	99	241
5[d]	$Pd(OAc)_2$	18	19	42
6[e]	**Pd-CNP-1**	18	34	81
7[C]	**Pd-CNP-2**	4	99	241
8[C]	**Pd-CNP-2**	2	38	93

[a] Reaction conditions: 1,4-dibromobenzene (1 mmol), $K_4[Fe(CN)_6]$ (0.34 mmol), dimethylformamide (DMF, 5 mL), 140 °C under nitrogen; [b] **Pd-CNP-1** (5 mg, Pd containing/0.00061 mmol); [c] **Pd-CNP-2** (5 mg, Pd containing /0.0041 mmol); [d] $Pd(OAc)_2$ (1.0 mg, Pd containing /0.0045 mmol); [e] **Pd-CNP-1** (34 mg, Pd containing /0.0042 mmol); [f] Yield was determined by ^{1}HNMR; [g] TON = mol of product / mol of catalyst.

Taken cumulatively, the combination of surface Pd sites, significant surface area, high loading, and greater accessibility to the putative catalytic site suggest that **Pd-CNP-2** could function as a highly active Pd catalyst for cyanation reactions.

To confirm this hypothesis, we subsequently carried out the cyanation of DBB to DCB using **Pd-CNP-2** as the heterogeneous catalyst. As expected, nearly full conversion (99 % yield) was achieved after heating at 140 °C for 18 h, with no additional base or stabilizing ligand added to the system (entry 6, Table 1). In contrast, the use of homogeneous $Pd(OAc)_2$ afforded a much lower yield (19 %) with a turnover number (TON) value of 42 (entry 5, Table 1), which are close to the previously-reported values.[3e] Furthermore, the excellent catalytic activity can also be maintained after heating for 4 h (entry 7, Table 1). These results clearly indicate that the catalytic cyanation activity of **Pd-CNPs** can be dramatically enhanced by spatial modulation of the intrinsic Lewis basic frameworks.

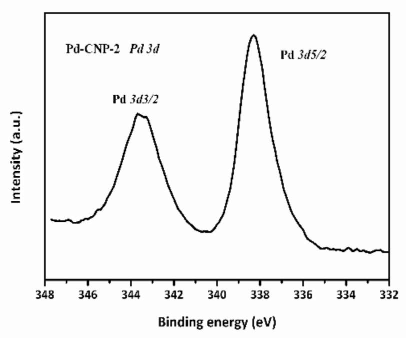


Figure 2. Pd 3d XPS spectra of **Pd-CNP-2**.

Recyclability is one of the most advantageous features of heterogeneous catalysts, particularly when precious metals are used.[3e] Accordingly, the reuse and stability of **Pd-CNP-2** was assessed for the model transformation of DBB to DCB. When simply collected by filtration, dried, and added to a new reaction, the recovered catalyst displayed negligible drop in activity after three recycles (**Figure 3a**), ICP analysis of the regenerated material reveals no significant change in Pd-content (Table S1), indicating excellent stability for the heterogeneous **Pd-CNP-2**. The morphology of **Pd-CNP-2** after the reaction maintains very well (Figure S5). It should be noted that the recyclability of **Pd-CNP-2** is better than that of **Pd-CNP-1** (Figure S6), which may be attributed to the stronger Pd-binding affinity of **Pd-CNP-2**. Furthermore, the reaction can be completely halted by removal of the **Pd-CNP-2**, confirming catalysis is performed by the material itself, and not by some unidentified solution-phase component (**Figure 3b**). Accordingly, these results show that the as-prepared nanoporous **Pd-CNP-2** is a robust and efficient heterogeneous catalyst for the cyanation reaction.

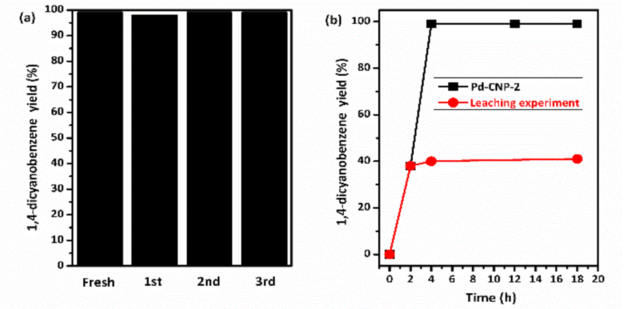


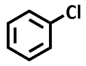
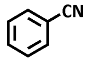
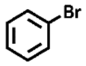
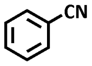
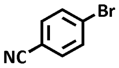
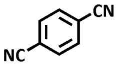
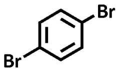
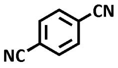
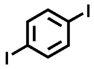
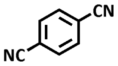
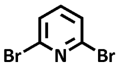
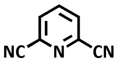
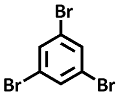
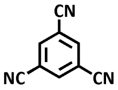
Figure 3. Pd-CNP-2 activity as a function of recycle (a) and leaching experiment (b) of **Pd-CNP-2** in the cyanation of DBB with $K_4Fe(CN)_6$.

Seeking to probe the generality of our **Pd-CNP-2** heterogeneous catalyst, we extended this new protocol to a range of other aryl halides. As shown in **Table 2**, these reactions generally afford full conversion to the desired benzonitriles, clearly demonstrating the diversity of this novel heterogeneous catalyst. It is worth noticing that this new approach shows great potential to convert other aromatic halides like less reactive chlorobenzene and tribromobenzene, which are generally difficult to be transformed under similar reaction conditions.[3e]

In conclusion, we have developed a novel heterogeneous system through spatially modulating the backbones of conjugated nanoporous polymers to achieve efficient and additive-free cyanation of aryl halides. The resulting catalyst displays high porosity, electron rich Pd(II)-containing active sites, and exhibits promising catalytic performance, including a high yield for all products, excellent recycle properties and stability, and a broad functional group tolerance. These exciting results demonstrate the great potential for application of metalated porous polymers in the context of heterogeneous catalysis.

Table 2. The cyanation of various aryl halides with $K_4[Fe(CN)_6]$ catalyzed by **Pd-CNP-2**.[a]

$$\text{Ar-X} + K_4[Fe(CN)_6] \xrightarrow[140^{\circ}C,\ 4h]{\text{Pd-CNP-2}} \text{Ar-CN}$$

Entry	Ar-X	Ar-CN	Yield (%)	TON
1			96	234
2			99	241
3			97	236
4			99	241
5			99	241
6			86	209
7			99	241

[a] reaction conditions: Ar-X (1 mmol), Pd-CNP-2 (5.0 mg, Pd containing /0.0041 mmol), DMF (5 mL) and K4[Fe(CN)$_6$] (0.17 mmol, entry 1-3; 0.34

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Keywords: Pd-metalated • Conjugated nanoporous polymers • additive-free • cyanation of aryl halides • spatial-modulation

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COMMUNICATION

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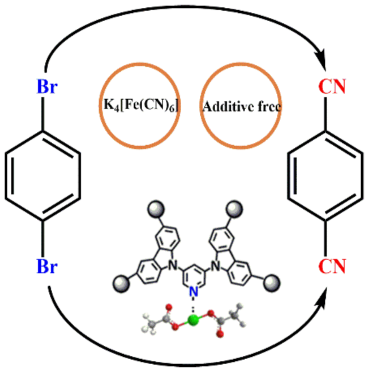

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