Palladium Nanocrystals-embedded Covalent Organic Framework (Pd@COF) as Efficient Catalyst for Heck Cross-Coupling Reaction
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Abstract
Nanoparticles, such as noble metal nanoparticles and covalent organic frameworks (COFs), advance heterogeneous catalysis. Three COFs were synthesized via the solvothermal method using tricarboxylic acids (tricarboxylic benzene (2,4,6-tri-p-carboxyphenylpyridine (H₃L2), 4,4′,4″-tri carboxyl triphenylamine (H₃L1), and trimesic acid (H₃BTC)) and 1,3,5-Triazine-2,4,6-triamine moieties. The synthesized COFs were potentially used as supports for the in-situ growth of palladium nanocrystals (Pd NCs), offering a particle size of 1-5 nm. X-ray diffraction (XRD), Fourier transforms infrared (FT-IR), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), nitrogen adsorption-desorption isotherms, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) characterized the materials. Using Heck cross-coupling reaction, Pd NCs@COFs were used as catalysts to synthesize different organic molecules via carbon-carbon (C-C) formation. They exhibit complete conversion (100%) for vinyl derivatives and aryl halides (Bromo- and Chloro-derivatives) with good stability. Pd NCs@COFs maintain high catalytic activity over four consecutive cycles.
**Keywords:** Covalent Organic Frameworks; COFs; Palladium Catalyst; Heck Reaction; Cross-coupling reaction.

**Introduction**

Covalent organic frameworks (COFs) are porous organic polymers [1–7]. They comprise lightweight elements (e.g., C, B, and N) linked via covalent bonds. They exhibited several advantages, including high chemical and thermal stability, high porosity, and low density [2,4,8–10]. Thus, they improved the performance for several applications such as gas adsorption or separation and catalysis [11–13]. COFs offer the potential to use as support and precursors for the synthesis of porous materials such as carbon nanomaterials [14–17].

Organic reactions via carbon-carbon (C-C) coupling are an important industrial method for synthesizing pharmaceuticals, drugs, and conjugated polymers [18–20]. The 2010 Nobel Prize in Chemistry was awarded to scientists Heck, Negishi, and Suzuki for developing palladium (Pd)-catalyzed C-C cross-coupling reaction [21–23]. Pd-based catalysts synthesize vital pharmaceutical drugs and valuable organic derivatives [24–26]. However, some reported catalysts require a high cost of ligands, difficult separation, and low recyclability. Various supports circumvent some of these challenges by preventing aggregation and offering several active Pd catalysts sites. The supports can be classified as natural materials (e.g., palygorskite[27], wool[28], halloysite[29]), inorganic (e.g., ZrO₂ [30], TiO₂ [31], CuO [32], CeO₂ [33], SiO₂ [34]), an organic polymer (e.g., chitosan [35], polyphenylene [36], and COFs [37–40]), and hybrid materials (e.g., metal-organic frameworks (MOFs) [41–46]). Among these supports, organic polymers, e.g., COFs, exhibit several advantages, such as high stabilization properties for Pd nanoparticles, preventing aggregation or agglomeration, high catalytic performance, and strong interactions [47,48].
Herein, we reported the synthesis of three different COFs materials using benzene-1,3,5-triamine and tricarboxylic acids, namely; tricarboxylic benzene 2,4,6-tri-p-carboxyphenylpyridine (H$_3$L2), 4,4',4''-tricarboxyltriphenylamine (H$_3$L1), and (trimesic acid, H$_3$BTC). The materials were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), high-resolution TEM (HR-TEM), Fourier transforms infrared (FT-IR), thermogravimetric analysis (TGA), and nitrogen adsorption-desorption isotherms. The materials were used to support the in-situ synthesis of Pd nanocrystals (Pd NCs) via reduction with sodium borohydride (NaBH$_4$)[49–54]. Pd NCs@COF exhibited good catalytic efficiency for the Heck reaction using a wide range of different substrates.

**Material and Experimental**

Methanol and dimethyl sulfoxide (DMSO) were purchased from SDFCL (India). Trimesic acid (H$_3$BTC), tetrahydrofuran (THF), palladium chloride (PdCl$_2$), sodium borohydride (NaBH$_4$), styrene, bromobenzene, chlorobenzene, 4-chlorobenzene, 2-chlorophenol, 4-bromoaniline, and 2-chlorobenzaldehyde were purchased from Sigma-Aldrich (Germany). Vinyl benzene (styrene) and methyl acrylate were purchased from Research-Lab Fine Chem Industries (India). 1,3,5-Triazine-2,4,6-triamine (melamine) was purchased from Merck (USA).

**Synthesis of tricarboxylic acids (H$_3$L1, H$_3$L2) and COFs**

**Synthesis of 4,4',4''-tricarboxyltriphenylamine (H$_3$L1)**

The synthesis of 4,4',4''-tricarboxyltriphenylamine (H$_3$L1) occurs via two steps, as shown in Figure S1. The procedures involved the synthesis of 4,4',4''-triacetyltriphenylamine followed by the oxidation using bromine in an alkaline solution (Figure S1).

**Synthesis of 4,4',4''-triacetyltriphenylamine**
A solution of acetyl chloride (28.28 mmol) was added dropwise to a mixture of triphenylamine (4.1 mmol) and AlCl₃ (13.5 mmol) in 150 mL of dry CH₂Cl₂. The reaction was then refluxed and stirred for 12 h. The reaction was diluted using H₂O (100 mL). The aqueous layer was extracted using CH₂Cl₂ (3×150 mL). The CH₂Cl₂ layers were dried using anhydrous Na₂SO₄. The solution was concentrated under reduced pressure before the purification via flash column chromatography using silica gel (pentane/CH₂Cl₂, 1:10).

**Synthesis of 4,4',4''-tricarboxyltriphenylamine**

Br₂ (3 mL) was added dropwise to a solution of sodium hydroxide (7.0 g NaOH (0.18 mol) was dissolved into 30 mL of H₂O), cooled on an ice bath, and further stirred for 20 min. The solution was transferred to a funnel for the addition dropwise to a solution of 4,4',4''-triacetyltriphenylamine (5.4 mmol) in 1,4-dioxane (50 mL) at 45 °C. The solution was acidified with HCl. The solid was separated via filtration and dried under a vacuum. The solid was recrystallized using acetic acid to afford a white solid.

**Synthesis of 2,4,6-tri-p-carboxyphenylpyridine (H₃L2)**

The synthesis of 2,4,6-tri-p-carboxyphenylpyridine (H₃L2) is schematically shown in Figure S2. The procedure steps involve the synthesis of 1,3-di-p-tolyl-propenone, 2,4,6-tri-p-tolylpyridine, and the oxidation using nitric acid (Figure S2).

**Synthesis of 1,3-di-p-tolyl-propenone**

A mixture of p-tolualdehyde (50 mmol), 4-methyl acetophenone (51 mmol), and aqueous sodium hydroxide (2%, 150 mL) was stirred at room temperature for 30 min before heating at 60 °C for six h. The reaction mixture was cooled to room temperature, and a light-yellow precipitate was filtered. The compound was washed with H₂O before drying.

**Synthesis of 2,4,6-tri-p-tolylpyridine**
4-Methylacetophenone (15 mmol), 1,3-di-p-tolyl-propenone (15 mmol), and powder NaOH (60 mmol) were added into a mortar and mixed with a pestle. A yellow powder was formed. It was mixed with an ammonium acetate solution (10 g, excess) in ethanol (100 mL). The reaction mixture was refluxed for ten-hour. The reaction solution was cooled to room temperature. The precipitate was filtered, washed with distilled water several times, and dried to give the product. The compound was purified using silica and elution with pentane/ethyl acetate (10:1).

**Synthesis of 2,4,6-tri-p-carboxyphenylpyridine (H₃L₂)**

2,4,6-tri-p-tolylpyridine (1.25 g, 3.58 mmol) was mixed with 10 mL diluted nitric acid (2 mL HNO₃ (63%) was added to H₂O (8 mL)) and heated in an autoclave at 160 °C for two days. The yellow solid was filtered and washed with water, ethyl acetate, and acetone. A light yellow solid of 2,4,6-tri-p-carboxyphenylpyridine was obtained.

The chemical structure of H₃L1 and H₃L2 was confirmed using proton nuclear magnetic resonance spectroscopy (¹H NMR, Bruker, 500 MHz) using Deuterated DMSO (Figure S3).

**Synthesis of COFs: COF-1, COF-2, and COF-3**

1,3,5-Triazine-2,4,6-triamine (21 mmol) was dissolved in anhydrous DMSO (25 mL) in a three-neck flask. The tricarboxylic acids, e.g., H₃L₂, H₃L₁, or H₃BTC (7 mmol), were added to the flask separately for the synthesis of COF-1, COF-2, and COF-3, respectively. The reaction mixture was refluxed at 150 °C for three days. Several times, the resultant precipitate was filtered and washed with hot water, THF, and methanol. The materials were further purified via extraction with acetone for 24 h. Finally, the yellow powders were dried under a vacuum at 80 °C for 24 h.

**Synthesis of Pd@COFs nanocomposites**

100 mg of COFs (e.g., COF-1, COF-2, and COF-3) and 100 mg of PdCl₂ were dispersed in 20 mL of distilled water via ultrasonication (for 30 min) and stirred overnight (10 h). Then, a methanol
solution of sodium borohydride (NaBH₄) was added to the suspension and stirred further at room temperature for one hour. A black precipitate was filtered and washed with methanol (1×20 mL) and water (2×20 mL). The materials were dried under vacuum for 24 h at 80 °C.

**General Procedure for Heck reaction Catalyzed by Pd NCs@COFs**

Heck reaction using several substrates was performed using a flask equipped with a magnetic stirrer. The reactants; aryl halides (1 mmol), olefines (1.5 mmol), trimethylamine (NEt₃, 1.5 mmol), DMSO (2 mL), and Pd NCs@COFs (5 mol%, 8.8 mg), were charged into the flask. The mixture was stirred at 100 °C for 24 h. Finally, the reaction mixture was cooled to room temperature. The catalysts were separated via filtration for the analysis. The reaction crude was analyzed using ¹H NMR.

**¹H NMR Characterization for Products:** 1,2-diphenylethene (1a), ¹H NMR (DMSO): δ = 7.2 - 7.6 (m, 10H), 7.8 - 8.2 (dd, 2H) ppm; 4-tyrylaniline (1b), ¹H NMR (DMSO): δ = 3.5 – 3.6 (s, 2H), 7.1 - 7.5 (m, 9H), 7.5 - 7.7 (m, 2H) ppm; 2-styrylphenol (1c), ¹H NMR (DMSO): δ = 4.5 – 4.6 (s, 1H), 6.5 - 7.2 (m, 9H), 7.2 - 7.6 (m, 2H) ppm; 4-styrylbenzaldehyde (1d), ¹H NMR (DMSO): δ = 7.0 - 7.7 (m, 9H), 7.7 - 7.9 (dd, 2H) ppm, 8.5 -8.8 (s, 1H); Methyl -2-methyl-3-phenylacrylate (1e), ¹H NMR (DMSO): δ = 2.9 – 3.2 (S, 3H), 4.8 – 5.0 (S, 3H), 7.1 - 7.15 (m, 5H), 7.15 - 7.2 (m, 2H); Methyl -3-(4-aminophenyl)-2-methylacrylate (1f), ¹H NMR (DMSO): δ = 2.6 – 2.8 (S, 2H), 2.8–2.9 (S, 3H), 5.0–5.1 (S, 3H), 6.7-7.5 (dd, 4H), 7.6 - 7.8 (m, 2H); Methyl -3-(2-hydroxyphenyl)-2-methylacrylate (1g), ¹H NMR (DMSO): δ = 2.4– 2.5 (S, 3H), 2.8–3.0 (S, 1H), 4.9–5.0 (S, 3H), 6.6 - 7.5 (dd, 4H), 7.5 - 7.8 (m, 2H); Methyl -3-(4-formylphenyl)-2-methylacrylate (1hj), ¹H NMR (DMSO): δ = 3.2– 3.4 (S, 3H), 5.0 – 5.1(S, 3H), 6.9-7.5 (dd, 4H), 7.8-8.0 (m, 2H), 9.6–9.8 (S, 1H); 4-styrylaniline (2b), ¹H NMR (DMSO): δ = 3.0–3.5 (s, 2H),
6.4-7.2 (m, 9H), 7.3-7.4 (dd, 2H) ppm; 4-styrylbenzaldehyde (2d), $^1$H NMR (DMSO): $\delta = 6.5$-7.2 (m, 9H), 7.4-7.6 (dd, 2H) ppm, 9.4 -9.5 (s, 1H); Methyl -3-(4-formylphenyl)-2-methylacrylate (2h), $^1$H NMR (DMSO): $\delta = 3.0$–3.2 (S, 3H), 4.8 – 5.0 (S, 3H), , 7.0 - 7.5 (dd, 4H), 7.6 - 7.9 (m, 2H), 9.7– 9.9 (S, 1H); 4-styrylaniline (3b), $^1$H NMR (DMSO): $\delta = 4.01$ – 4.3 (s, 2H), 7.1 - 7.2 (m, 9H), 7.3 - 7.4 (dd, 2H) ppm; 4-styrylbenzaldehyde (3d), $^1$H NMR (DMSO): $\delta = 7.2$-7.5 (m, 9H), 7.6-7.9 (dd, 2H) ppm, 9.9-10.1 (s, 1H); Methyl -3-(4-formylphenyl)-2-methylacrylate (3h), $^1$H NMR (DMSO): $\delta = 2.9$–3.1 (S, 3H), 4.6–4.9 (S, 3H), 7.0 - 7.7 (dd, 4H), 7.8–8.0 (m, 2H), 9.8–10.0 (S, 1H), Methyl -3-(4-aminophenyl)-2-methylacrylate (3f), $^1$H NMR (DMSO): $\delta = 2.5$–2.7 (S, 2H), 2.7–2.8 (S, 3H), 5.1–5.2 (S, 3H), 6.6-7.7 (dd, 4H), 7.8 - 7.9 (m, 2H)

**Instruments**

The X-ray diffraction (XRD) patterns were recorded using a Philips PW1700 diffractometer (Netherlands, Cu Kα). The transmission electron microscope (TEM) and high resolution-TEM (HR-TEM) images were performed using JSM-2100 (JEOL, Japan). Fourier transforms infrared (FT-IR) spectra were recorded using a Nicolet model 6700 spectrophotometer (Thermo Fisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Thermo Fisher (K-alpha, Al Kα radiation). The thermogravimetric analysis (TGA) was performed using PerkinElmer TGA T60 under a nitrogen atmosphere. Nitrogen adsorption-desorption isotherm was recorded using Quantachrom (Model Nova 3200, USA) at 77K. $^1$H NMR spectra were recorded using 500 MH (JEOL, Japan). Gas chromatography-mass spectrometry was performed using GC-MS (Thermo Scientific) connected to a single quadrupole mass spectrometer (ISQ 7000). The mass spectra were recorded using electron impact mode. The UV-Vis diffuse reflectance spectroscopy (DRS) of solid samples was measured using the Evolution 220 spectrophotometer (Thermo Fisher Scientific, UK).
Results and Discussion

Materials Characterization

A schematic representation for the synthesis of COF-1, COF-2, and COF-3 is shown in Figure 1. The synthesis procedure involves condensing tritopic carboxylic acids (e.g., H$_3$L$_2$, H$_3$L$_1$, or H$_3$BTC) and 1,3,5-Triazine-2,4,6-triamine. The materials are purified and characterized using XRD (Figure 2a), FT-IR (Figure 2b), DRS (Figure 3), XPS (Figure 4), TEM and HR-TEM images (Figure 5), TGA (Figure S4), and nitrogen adsorption-desorption isotherms (Figure S5).

Figure 1 The synthesis procedure of COFs and Pd@COFs. The inset image represents the HR-TEM image of Pd NCs with a diameter of 4 nm.
XRD patterns for COFs materials are shown in Figure 2a. No sharp peaks indicate the low crystallinity of the prepared materials (Figure 2a). The FT-IR spectra of the 1,3,5-Triazine-2,4,6-triamine and COFs materials are shown in Figure 2b. After COF formation, the functional groups in 1,3,5-Triazine-2,4,6-triamine groups are significantly changed due to amide groups (-NH-CO-). The bands at a wavenumber of 2815 cm$^{-1}$ and 2700 cm$^{-1}$ refer to =C-H stretching of the aromatic ring. The strong peak at 1715 cm$^{-1}$ refers to the carbonyl group. The FT-IR spectra of COF show a band at 3380-3385 cm$^{-1}$ is attributed to the N-H symmetric stretching vibration. The broad band around 1683-1680 cm$^{-1}$ is assigned to the C=O stretch of the amide group (Figure 2a).

![Figure 2](image-url)  
**Figure 2** Characterization of COFs using a) XRD and b) FT-IR.
The optical properties of the prepared materials were characterized using DRS spectra (Figure 3). 1,3,5-Triazine-2,4,6-triamine (melamine) and H$_3$L$_2$ were recorded to compare with COFs materials (Figure 3). Melamine and COF-3 are white color materials; thus, they show absorbance peaks at 230 nm and 239 nm (Figure 3). The shift in the absorbance peaks in COF-3 indicates the formation of a framework containing melamine (Figure 3). Nitrogen-containing ligand and their COFs are yellow-orange color materials; thus, they show an absorbance peak at 360-370 nm (Figure 3). There is also a shift in the absorbance of H$_3$L$_2$ after the formation of COF-3, indicating the condensation with melamine moiety (Figure 3).
Figure 3 DRS spectra of COFs and their moieties.

The chemical bonds of COF-1 were further characterized using XPS (Figure 4). The elemental XPS survey shows only elements of C, N, and O (Figure 4a). The XPS analysis of C 1s shows peaks at binding energies (BE) of 284 eV, 288 eV, and 290 eV corresponding to C–C, -C=O, and -C-O, respectively (Figure 4b). The analysis of N 1s shows peaks at BE of 398.7 eV, 400 eV, and 402 eV corresponding to N-C of the amide group, C=N of pyridine, and C=N triazine ring, respectively (Figure 4c). O 1s spectrum shows peaks at 531.5, 534, and 536 eV corresponding to C=O, C-O-H, and N=C-O, respectively (Figure 4d).
The thermal stability of the prepared materials was characterized using TGA (Figure S4). The material exhibits thermal stability up to 350 °C and 425 °C for COF-3, and COF-1/COF-2, respectively (Figure S4). Nitrogen adsorption-desorption isotherms confirm the presence of porous materials (Figure S5). In general, polyamide exhibits low surface areas for several reasons, including the non-planar configuration of the bond [55,56]. Thus, the prepared COFs can be used as a substrate for the in-situ synthesis of palladium nanoparticles. The synthesis procedure for Pd involves adding and reducing Pd$^{2+}$ ions via an in-situ approach (Figure 1).

The particle sizes and morphology of COFs and Pd@COFs were characterized using TEM images (Figure 5). TEM images of COF-1 and COF-2 show particles with a size distribution of

Figure 4 XPS analysis of COF-1, a) survey, b) C 1s, c) N 1s, and d) O 1s.
25-110 nm and 25-55 nm, respectively. COF-1 exhibits a larger particle size than COF-2 because of the length of the tricarboxylic acid. COFs materials tend to aggregate and create inter-particle pores that were confirmed from nitrogen adsorption-desorption isotherms. TEM images for Pd-COFs materials show the presence of dark particles corresponding to the palladium particles (Figure 5c-d). The data show the homogenous distribution of Pd into COF-1 and COF-2. The particle size distribution of Pd was calculated using TEM images that show a particle size distribution of 1-5 nm with an average particle size of 2.6 nm (Figure 5c-d).

![TEM images for a) COF-1, b) COF-2, c) Pd@COF-1, and Pd@COF-2, inset for a-b) and c-d) show the particle size distribution for COF-1/COF-2 and Pd, respectively.](image)

**Figure 5** TEM images for a) COF-1, b) COF-2, c) Pd@COF-1, and Pd@COF-2, inset for a-b) and c-d) show the particle size distribution for COF-1/COF-2 and Pd, respectively.

Pd NCs embedded COFs were synthesized via the in-situ reduction of palladium ions using the hydrogen generated via the methanolysis of NaBH₄ at room temperature[57]. High-resolution
TEM images of the dark particles are recorded for Pd@COF-1 and Pd@COF-2 (Figure 6a-b). They show well-defined lattices indicating the high crystallinity of the small dark particles. HR-TEM images exhibit lattice fringes of distance 0.23 nm corresponding to the Miller index of (111) of Pd nanocrystals (Figure 6c-d). Data confirm the successful synthesis of palladium nanocrystals (Pd NCs) into COFs materials.

![HR-TEM images](image-url)

**Figure 6** HR-TEM image for a, c) Pd@COF-1 and b, d) Pd@COF-2. The white circle represents the particles shown in the c and d images.

**Cross-coupling using Pd NCs@COFs**

Pd NCs@COFs were used as catalysts for C-C cross-coupling via Heck's reaction (Scheme 1). The reaction involves the reaction of vinyl derivatives with aryl halides in the presence of trimethylamine (Et₃N) and Pd NCs@COFs as heterogeneous catalysts. Several substrates were
investigated as tabulated in Table 1. The conversion was calculated using $^1$H NMR (Figure 7, Figure S6-S9). In the presence of Pd NCs@COFs (5 mol% of Pd), the desired adduct was obtained in high conversion (100%, Table 1). Chloro- and bromobenzene derivatives were used without and with other functional groups such as formyl (CHO), hydroxyl (O-H), and amine (NH$_2$). Vinyl benzene (styrene) and vinyl ester (methyl acrylate) were tested. All aryl halide and vinyl derivatives exhibit high conversion (Table 1), indicating the high catalytic performance of Pd NCs@COFs.

Scheme 1 C-C coupling via Heck's reaction.

$^1$H NMR spectra show no presence of any reactants indicating the complete conversion (Figure 7). The peak assignments are suitable matches with the expected NMR signals. The highest peak corresponds to the solvent peak, i.e., DMSO. The active functional groups such as formyl show no side reactions such as oxidation (i.e., COOH) or reduction (i.e., -CH$_2$OH), indicating that the reaction condition is mild for substrates with active functional groups. The presence of electron-donating groups (e.g., NH$_2$, OH) or electron-withdrawing groups in the substrate significantly
affects the catalyst's conversion. This observation indicates that Pd NCs@COFs catalysts can be further used for a wide range of different substrates.

The molecular weight of the products was also further confirmed using mass spectrometry (MS, Figure S10-S11). The peak corresponding to the parent peak ensures the molecular weight for 1c and 1e products at m/z 195 and 208, respectively. The product's structure can be approved from the fragmentation (Figure S10-S11). The base peak at m/z 91 for both products is assigned to tropylium ions, which exhibit high stability due to forming a seven-member ring. MS spectra confirm the formation of the desired product via cross-coupling reactions (Table 1).
Figure 7 $^1$H NMR spectra of 1, 2, and 3 (c, e, and j). Insets represent the enlarged area of NMR spectra.
Table 1 Summary for C-C coupling reaction using different substrates.

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The mechanism of Heck reaction using Pd NCs@COFs is schematically shown in Figure S13. The reaction involves oxidative addition, insertion, rearrangement, and reductive elimination (Figure S12). The presence of COFs with benzene rings and amide functional groups could enhance the interaction with the substrate via several non-covalent bonds leading to high catalytic performance.

The recyclability of the catalysis using Pd NCs@COF catalysts was investigated, as shown in Figure S13. All runs were performed under identical reaction conditions. As a heterogeneous Pd NCs@COF catalyst, the solid catalyst can be easily separated via filtration or centrifugation after each run, washed with ethanol, and dried for the next catalytic run. The catalytic conversion is over 95% even after the 4th cycle, suggesting excellent recyclability of Pd NCs@COF catalysts. This observation indicates that Pd NCs@COF catalysts maintain their catalytic performance after the reaction without observing metal leaching in the reaction solution.

Pd NCs@COFs offer several advantages for being a catalyst for C-C cross-coupling. The catalyst exhibits high catalytic activity with complete conversion. It can be used for a wide range of different substrates. The synthesis procedure for the palladium nanocrystals is straightforward. It

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requires the addition of the metal salts into the COFs materials that enable coordination to palladium (Pd\textsuperscript{2+}) ions before the in-situ reduction to Pd\textsuperscript{0}. The presence of nitrogen into the COFs frameworks enhanced the stability of Pd NCs\cite{58}. Thus, there is no dramatic change in the catalyst performance for several runs. There is no observation for palladium leaching during the reaction.

**Conclusions**

Pd NCs@COFs catalysts were synthesized using a facile synthesis procedure via in-situ method at room temperature. They were used as catalysts for cross-coupling reactions using the Heck reaction. The catalytic performance of Pd NCs@COFs nanocomposite showed complete conversion (100\%) with five mol.% of Pd NCs. The high conversion was observed for several aryl halides and vinyl derivatives. We expect these catalysts to be viable for synthesizing several more new organic compounds via cross-coupling reactions using Pd-based catalysts.

**Reference**


J. Mondal, A. Modak, A. Bhaumik, One-pot efficient Heck coupling in water catalyzed by


