

Hyperbranched Polymer Immobilized Palladium Nanoparticles as an Efficient and Reusable Catalyst for Cyanation of Aryl Halides and Reduction of Nitroarenes

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Abstract

A new nitrogen-rich hyperbranched polymer comprising imidazolium and triazole moieties used for stabilization of Pd nanoparticles. The resulting new material, PolyTZ-IL@Pd NPs, was characterized with different techniques including Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-Ray (EDX), and transmission electron microscopy (TEM) analysis. PolyTZ-IL@Pd NPs has been used as an efficient catalyst in the reduction of nitroarenes to amines and cyanation of aryl bromides and iodides. The catalyst showed high stability and recyclability and recycled at least 10 times in reduction of 1-chloro-4-nitrobenzene and 5 times in cyanation of iodobenzene.

Keywords: Polymer, Palladium, Nano-catalyst, Reduction, Cyanation

1. Introduction

Heterogeneous catalysts with high surface area, easy recovery and separation from the products have received great attention in industrial chemical production. Different ligands and functional groups especially phosphorus and nitrogenous ligands were used for preparation of the various heterogeneous catalysts. However, compared to phosphorus ligands which are usually toxic, expensive and thermally unstable, less toxic, cheap and easily synthesis nitrogenous ligands are more attractive [1-3].

The wide range of synthetic applications of heterogeneous palladium catalysts includes various examples of cross-coupling [4-7] and reduction reactions [8-10]. Among the latter, one of the most significant transformation is the reduction of nitro compounds to amines. Amines are important class of organic compounds and useful precursors in synthesis of structurally diverse materials such as pharmaceuticals, corrosion inhibitors, surfactants, dyes, polymers and agrochemicals [11, 12]. One of the efficient methods for the preparation of amines include the reduction of corresponding nitro compounds which are considered as toxic and industrial wastes materials. Compared to classic methods such as Bechamp reduction [13] which are time consuming, and reactions conducted in harsh acidic conditions producing large amounts of waste, catalytic hydrogenation using transition metals catalyst is highly clean, efficient and compatible with industrial applications. Among different metals used for reduction of nitro groups, Pd catalysts catalyze this reaction very efficiently with the formation of fewer by-products [14-26].

It is worth mentioning that compared to other Pd catalyzed C-C bond formations less attention have been paid to catalytic cyanation reaction. Aromatic nitriles have various applications in pharmaceuticals, agrochemicals, dyes, and pigments industries. On the other hand, nitrile can be transferred to various functional groups such as aldehydes, amines, amidines, tetrazoles, carboxylic acids, and carboxylic acid imidoesters, benzamidines, and nitrogen-containing heterocycles [27, 28]. Traditional methods for synthesis of aryl nitriles include Rosenmund-von Braun [29, 30] and Sandmeyer [31-35] reactions which have drawbacks of using stoichiometric CuCN at harsh reaction conditions. To overcome these disadvantages, nowadays nucleophilic cyanation of aryl halides was performed using transition metals such as Pd [36-50], Ni [51] and Cu [52, 53] under efficient conditions.

Among the different solids for preparation of recyclable catalysts, organic polymers [54] having unique properties such as easy preparation steps, tunable hydrophilic–hydrophobic character and high loading of desired functional group are excellent materials for depositing metal nanoparticles [55]. Earlier, we reported about preparation heterogeneous palladium catalysts via immobilization of palladium(II) acyclic diaminocarbene (Pd(II)-ADC) complexes on resin support by metal-mediated addition of amino groups of benzhydrylamine-polystyrene to the coordinated isocyanide ligand of *cis*-PdCl₂(CNR)₂ (R = *t*-Bu, Cy). Resin-supported palladium catalysts obtained demonstrated high catalytic activity in both Sonogashira-Hagihara and Suzuki–Miyaura cross-coupling [56].

In this work, a new branched polymer having as a core 2,4,6- substituted *s*-triazine, and inside chains triazole and imidazolium moieties, has been prepared and used for stabilization of Pd NPs. The resulting new heterogeneous catalyst showed high catalytic activity both in the cyanation of aryl halides and the reduction of aromatic nitro compounds in an H₂O/Ethanol medium.

2. Experimental Section

2.1 Materials and methods

All materials were purchased from Sigma-Aldrich, Acros and Merck. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60F254 glass plate with 0.25 mm thickness and Varian CP-3800 gas chromatograph. Column chromatography was carried out on silica gel 60 Merck (230-240 mesh) in a 2 cm diameter column. ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz, respectively on Bruker Avance HD. Chemical shifts are given on the δ-scale in ppm, and residual solvent peaks were used as internal standards. X-ray diffraction (XRD) patterns were recorded using Philips X'Pert Pro instrument. The TEM and SEM images were captured with EOL JEM-2010 and JEOL JSM 840, respectively. X-ray detector Bruker XFlash 3001 was used with SEM equipment for microanalysis (EDS) and mapping. XPS analyses were performed using a K-Alpha spectrometer. Most yields were calculated by GC. Moreover, some products' progression was evaluated by isolated yields in which column chromatography was used as purification technique and by weighing the number of pure products.

2.2 Synthesis of 2,4,6-tris(prop-2-yn-1-yloxy)-1,3,5-triazine (Scheme 1, A1)

In a 50.0 mL flask containing 2,4,6-trichloro-1,3,5-triazine (2.0 mmol, 0.37 g), anhydrous THF (10.0 mL) and propargyl alcohol (8.0 mmol, 0.46 mL) were added and mixture was stirred under argon atmosphere for 10 min at 0 °C. Then, sodium hydride 60% (20.0 mmol, 0.48 mg) was added quickly under argon protection and the whole mixture was stirred at 0 °C for 1 hour. Then, the reaction temperature was allowed to reach room temperature and further stirred for 24 h. Afterward, the mixture was filtered and the THF was evaporated, and the product was extracted by water (20 mL) and dichloromethane (3×10.0 mL). The resulting organic layer was dried over anhydrous sodium sulfate and it was evaporated. At the end 2,4,6-tris(prop-2-yn-1-yloxy)-1,3,5-triazine was achieved in 84% yield.

2.3 Synthesis of 1-(3-chloropropyl)-1H-imidazole (Scheme 1, A2)

In a 50.0 mL 1H-imidazole (12 mmol, 817 mg) and THF (10 mL) were added, and mixture stirred at 0 °C for 30 min. Then sodium hydride 60% (20.0 mmol, 0.48 g) was added quickly under argon protection and the mixture was stirred for 1 h under argon atmosphere. Then, 1-bromo-3-chloropropane (10.0 mmol, 0.98 mL) was added and reaction temperature was allowed to reach room temperature. The reaction was stirred at room temperature for 24 h. Afterward, mixture was filtered and the THF was evaporated. The product, 1-(3-chloropropyl)-1H-imidazole (2), was extracted by water (20 mL) and ethyl acetate (2×10.0 mL).

2.4 Synthesis of 1,3-bis(3-chloropropyl)-1H-imidazol-3-ium bromide (Scheme 1, A3)

To a flask containing 1-(3-chloropropyl)-1H-imidazole (10 mmol, 1.4 mL) and 1-bromo-3-chloropropane (10.0 mmol, 1 mL) were added and the mixture was stirred at temperature for 48 h. Then, the resulting mixture was washed several times with ethyl acetate and obtained IL (3) was dried in the oven at 60 °C.

2.5 Synthesis of TZ-ILs (Scheme 1, A4)

In a 50.0 mL flask containing sodium azide (30.0 mmol, 1.95 g) and 1,3-bis(3-chloropropyl)-1H-imidazol-3-ium bromide (10.0 mmol, 3.0 g), acetone (15 mL) and deionized water (5.0 mL) were added, and the mixture was stirred under reflux (70 °C) for 24 h. Then, 2,4,6-tris(prop-2-yn-1-yloxy)-1,3,5-triazine (6.60 mmol, 1.60 g) was added to the mixture. In another flask, 10.0 mL flask copper (II) sulfate (0.50 mmol, 80.0 mg), ascorbic acid (1.5 mmol, 264.0 mg), acetone (1.50 mL) and deionized water (0.50 mL) were added, then the obtained solution was added slowly to the previous reaction mixture. The resulting mixture was stirred under reflux (70 °C) for 24 h. Afterward, the solvent was evaporated and to the resulting solid H₂O (1 mL) and EtOH (15 mL) were added and reaction mixture decanted off. Resulting solid washed with EtOH (10 mL) and dried in oven at 60 °C.

2.6 Preparation of polymer-supported Pd catalyst (TZ-IL@Pd NPs) (Scheme 1, A5)

In a 25.0 mL flask, absolute ethanol (10.0 mL) was added to polymeric support (1.0 g) while stirring. In another flask, Pd(OAc)₂ (0.05 mmol, 11 mg) was dissolved in absolute ethanol (2.0 mL) and slowly added to the polymeric support mixture at room temperature under argon atmosphere. Then, sodium borohydride (1.0 mL of 0.8 M) solution was prepared, and it was added to the mixture dropwise while stirring. The time interval for each drop was 2 min. After 12 h stirring, the reaction mixture was transferred to a 15.0 mL falcon and centrifuged at 4000 rpm for 10 min and resulting solid was washed with a mixture of water: ethanol (1: 10) and dried in vacuum oven. The loading of Pd on the obtained material was determined by atomic absorption spectroscopy (AAS) to be 0.02 mmol·g⁻¹.

2.7 General procedure for the catalytic reduction of nitro compounds using TZ-IL@Pd NPs catalyst

To a 5 mL glass flask, nitroarene (0.5 mmol), NaBH₄ (2.0 mmol, 75.50 mg), catalyst TZ-IL@Pd NPs (12.5 mg, 0.05 mol% of Pd), H₂O (0.15 mL) and ethanol (1.35 mL) were added. The reaction mixture was stirred for an appropriate reaction time at room temperature. The progress of the reactions was monitored by GC or TLC. After the completion of the reaction, the product was extracted by ethyl acetate (3×5.0 mL) and further purified with column or plate chromatography using hexane and ethyl acetate as eluents.

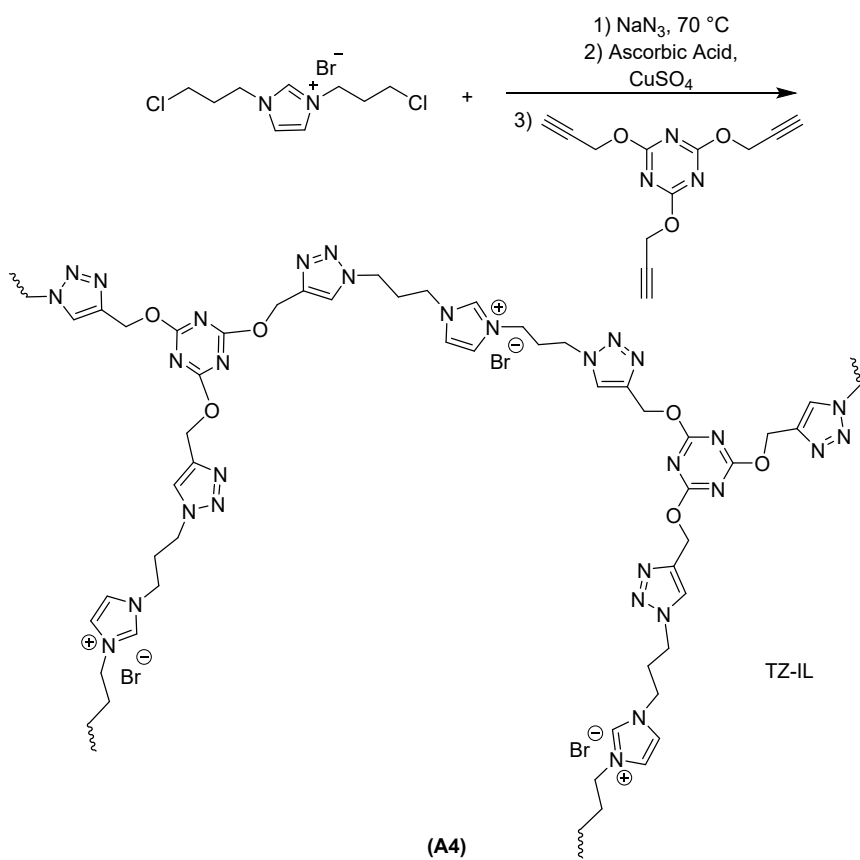
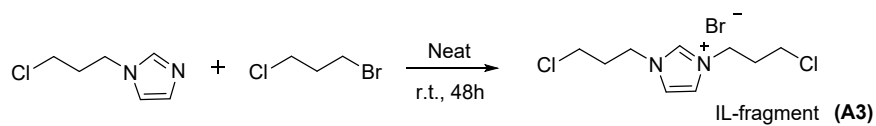
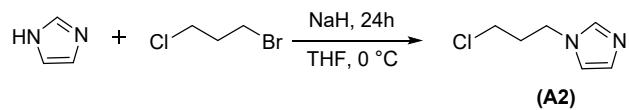
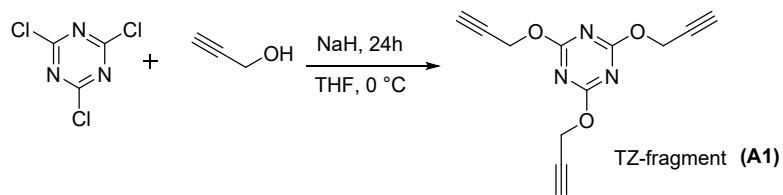
Hint: Amine products are mostly unstable, and it is necessary to keep the products in the refrigerator and under argon atmosphere. Do not let the products exposed to air for extended time.

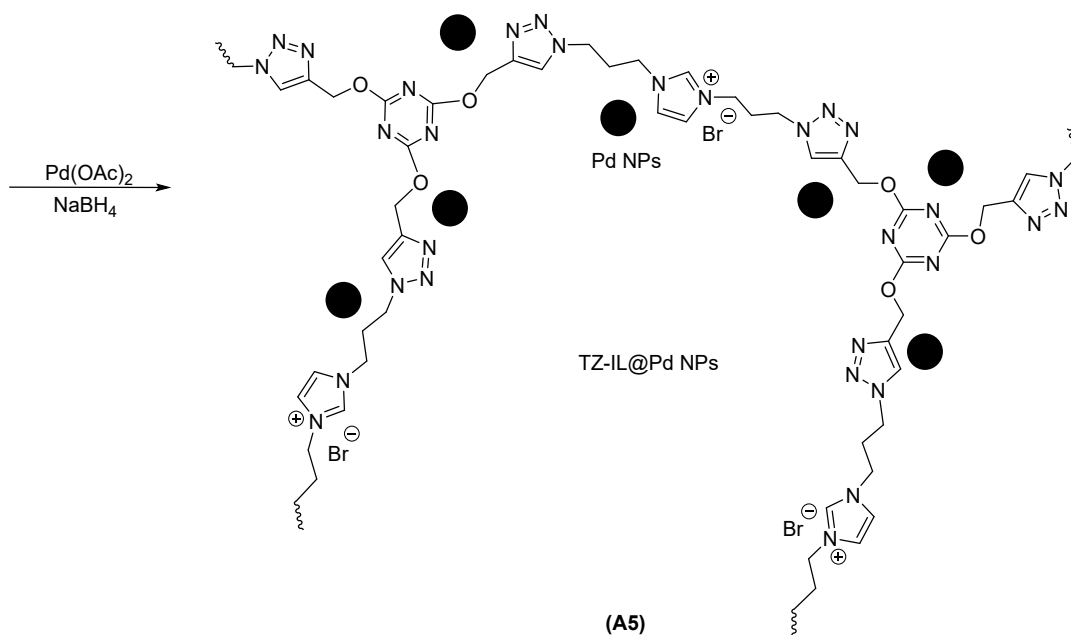
2.8 General procedure for the catalytic cyanation of different aryl iodides and bromides

Catalyst (25 mg, 0.1 mol% of Pd), Na₂CO₃ (0.75 mmol), aryl halides (0.5 mmol), K₄Fe(CN)₆ (0.3 mmol) and DMF (2.0 mL) were added to a reaction tube and stirred at 120°C for the appropriate reaction time. The progress of the reactions was monitored by GC. After the completion of the reaction, the reaction mixture was cooled to room temperature and H₂O (3.0 mL) was added to the mixture and the crude product was extracted with ethyl acetate (3 × 5.0 mL) and further purified with column or plate chromatography using hexane and ethyl acetate as eluents.

3. Results and discussion

s-Triazine, as a nitrogen-rich heterocyclic ring, is a very useful platform for the construction of structurally different molecules and stepwise substitution reactions [57-59]. When designing support for the Pd-catalyst, we decided to use s-triazine (TZ) as the central core and introduce imidazolium (IL) fragments into the side chains using click reaction of azide with terminal triple bond. Initially propargyl alcohol was reacted with 2,4,6-trichloro-1,3,5-triazine in the presence of NaH as a base to give 2,4,6-tris(prop-2-ynyloxy)-1,3,5-triazine (TZ-fragment) in 78% yield (Scheme 1, A1). The preparation of IL-fragment, imidazole was alkylated with 1-bromo-3-chloropropane using NaH as a base in dry THF (Scheme 1, A2). Subsequent reaction of obtained 1-(3-chloropropyl)-1H-imidazole with a second equivalent of 1-bromo-3-chloropropane affording IL-fragment (Scheme 1, A3). Structures of 2,4,6-tris(prop-2-ynyloxy)-1,3,5-triazine TZ and IL were characterized by ¹H and ¹³C NMR spectroscopies. The next step involved the click reaction between IL and 2,4,6-tris(prop-2-ynyloxy)-1,3,5-triazine using CuSO₄ and sodium ascorbate. Obtained polymer was treated (Scheme 1, A4) with Pd(OAc)₂ followed by reduction with NaBH₄ to afford new polymer-supported Pd NPs (TZ-IL@Pd NPs) (Scheme 1, A5). Using atomic absorption spectroscopy, the loading of Pd in the Starch-Fe₃O₄@IL-TZ-Pd was found to be 0.02 mmol.g⁻¹.





Scheme 1. Steps for preparation of TZ-IL@Pd NPs

Structure of TZ-IL@Pd was studied with FTIR spectroscopy (Fig. 1). In IR spectrum peak at 3090 is related to stretching vibration of C=C–H of the 1,2,3-triazole. Also, peaks located at 1660, 1400-1600, 1480-1440, 1050-1250, 650-900 cm^{-1} are related to stretching vibration of C=N, aromatic stretching of C=C, CH_2 bending vibration, C–O–C stretching vibration, and C–H bending vibration, respectively [60-62].

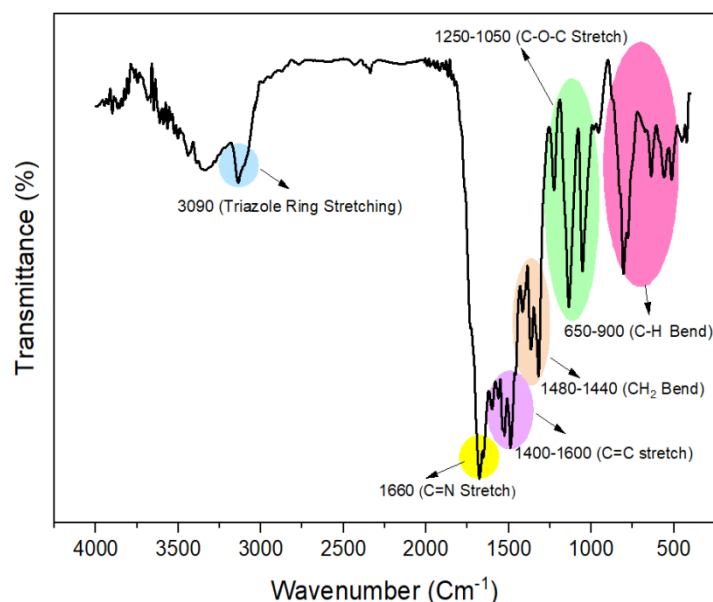


Fig. 1 FT-IR spectra of TZ-IL@Pd

X-ray diffraction (XRD) analysis of TZ-IL@Pd NPs showed formation of Pd(0) nanoparticles by appearing Bragg's reflections related to palladium in $2\theta = 40.1, 46.7, 68.1$ (Fig. 2) [63].

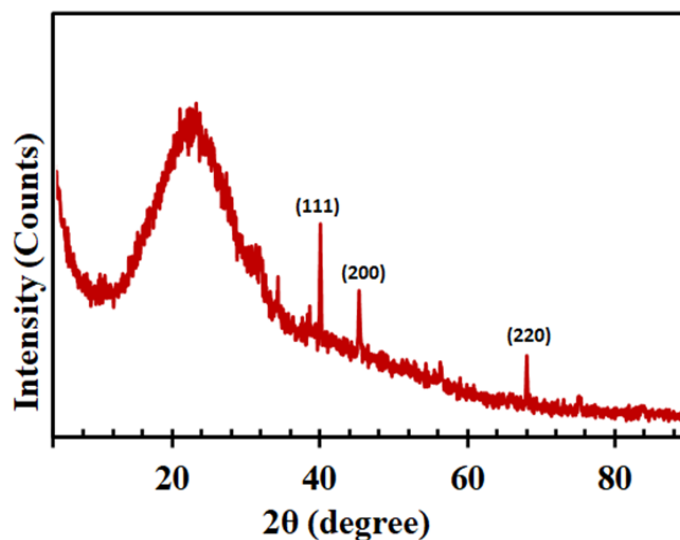


Fig. 2 XRD pattern of the TZ-IL@Pd NPs

In order to investigate the surface chemistry of the supported Pd, X-ray photoelectron spectroscopy (XPS) was used (Figure 3). XPS spectra in N 1s region showed three peaks centered at 398.6, 400.0 and 401.6 which are related to N=N, N-C and quaternary nitrogen, respectively (Fig. 3a) [64, 65]. Appearance of Br 3d_{5/2} and Br 3d_{3/2} doublet at 67.2 and 68.2 confirmed presence of Br in the structure (Fig. 3b) [66, 67]. XPS results in C 1s region showed four peaks located at 284.3, 285.4, 286.4, and 288.5 that correspond to carbons in C=C, C-C, C-O, and C=O moieties, respectively (Fig. 3c) [68]. XPS spectrum of Pd showed two doublets related to Pd3d_{5/2} and Pd 3d_{3/2}. Peaks centered at 335.2 and 340.5 are assigned to Pd(0) and peaks located at 337.3 and 342.5 eV are associated with Pd(II) species (Fig. 3d) [69].

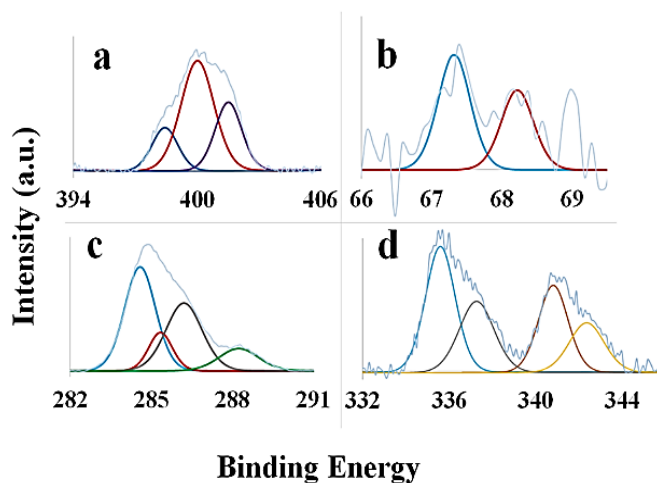


Fig. 3 XPS spectra of TZ-IL@Pd NPs in a) N, b) Br, c) C, d) Pd regions.

As can be seen in Fig. 4 presence of different elements such as Pd, N, has been also confirmed by the energy dispersive X-ray (EDX) analysis. The analysis indicated 0.9% of Pd in the structure.

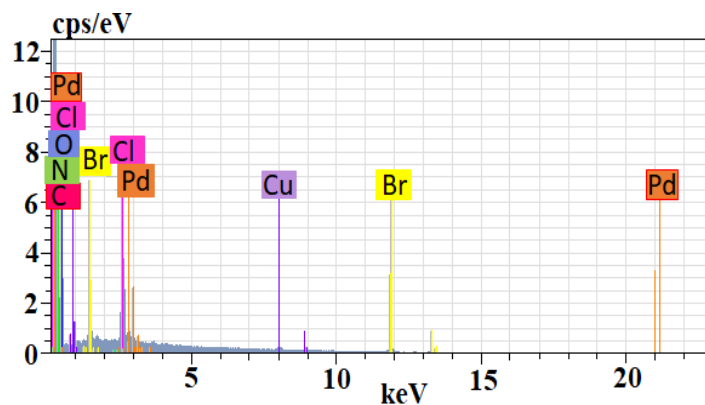


Fig. 4 EDX spectrum of TZ-IL@Pd NPs

Results of transmission electron microscopy (TEM) studies in different magnification indicate a presence of distribution almost uniform Pd NPs over the support. Particle size distribution plot obtained from TEM measurements exhibited that major portions of the Pd NPs particles are found between 4-8 nm (Fig. 5).

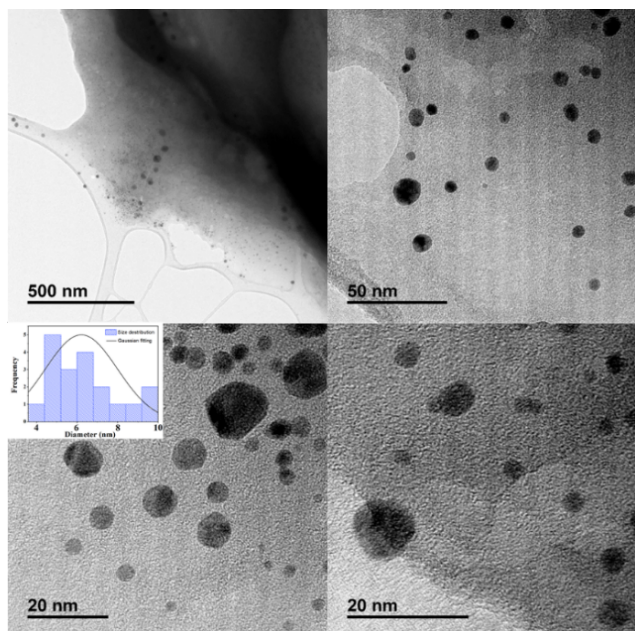
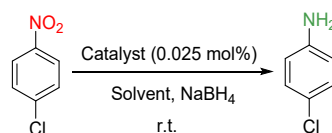


Fig. 5 TEM images and size distribution graph of TZ-IL@Pd NPs in different magnifications.

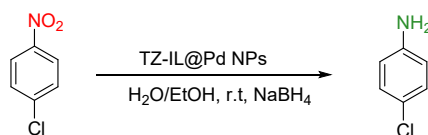
Catalytic application of TZ-IL@Pd NPs was studied in two important organic transformations such as nitro group reduction and cyanation of aryl halides. In order to find optimized reaction conditions of the nitroarenes reduction, 1-chloro-4-nitrobenzene was selected as the model compound and effect of the reducing agent and solvent nature, as well as catalyst amount was investigated (Table 1). Results showed that using 0.025 mol% of catalyst, NaBH₄ (4eq) as reducing agent in H₂O and EtOH gave 39 and 43% yields (Table 1, entries 1 and 2), respectively while using mixture of H₂O/EtOH (1:10), 56% yield was obtained during 15 min (Table 1, entry 3). Performing reactions in other solvents led to lower yields (Table 1, entries 4-12).

Table 1. Reduction of 1-chloro-4-nitrobenzene using 0.025 mol% of catalyst in different solvents^a

Entry	Solvent	Yield (%) ^[b]
1	H ₂ O	39
2	Ethanol	43
3	H ₂ O/Ethanol (1:10)	56
4	1,4-Dioxane	7
5	PEG-200	19
6	DMF	13
7	THF	15
8	Ethyl acetate	28
9	Toluene	<5
10	Acetone	22
11	DMSO	40
12	Dichloromethane	8

^a Reaction condition: 1-chloro-4-nitrobenzene (0.5 mmol), catalyst (6 mg, 0.025 mol% of Pd), solvent (1.5 mL), NaBH₄ (4 eq) at room temperature. ^b GC yields.

Aqueous EtOH was chosen as a solvent for further investigation of the effect of the catalyst and NaBH₄ amount on the yield of aniline. When the amount of catalyst was increased to 0.035 and 0.05 mol%, the yields were 81 and 97% (Table 2, entries 1, 2). Results showed that with decreasing NaBH₄ amount to 3 and 2 equivalents, yields of 4-chloroaniline were reduced to 82 and 67%, respectively (Table 2, entries 3, 4). Using 0.05 mol% catalyst and 4eq NaBH₄ in shorter reaction time gave low yields (Table 2, entry 5). It is worth mentioning that reaction in the absence of catalyst or NaBH₄ failed to proceed and 5 and 2% yields were obtained, respectively (Table 2, entries 6, 7).

Table 2. Effect of catalyst and NaBH₄ amounts in the reduction of 1-chloro-4-nitrobenzene ^a.

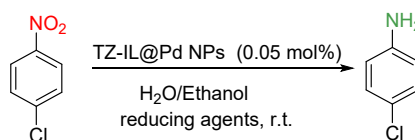
Entry	Catalyst (mol%)	NaBH ₄ (eq)	Time (min)	Yield (%)
1	0.035	4	15	81
2	0.05	4	15	97
3	0.05	3	15	82

4	0.05	2	15	67
5	0.05	4	8	65
6	----	4	15	5
7	0.05	---	15	2

^a GC yields

Then we focused on the effect of various reducing agents on the reduction of 1-chloro-4-nitrobenzene (Table 3). Obtained results showed that using other reducing agents such as ammonium formate, formic acid, isopropyl alcohol, hydrazine, and glycerol very low yields were achieved (Table 3, entries 1-5). Briefly, results presented in Tables 1-3 indicated that using 0.05 mol% of catalyst, aqueous EtOH as a solvent, 4 eq of NaBH₄ is the most efficient conditions for the reduction of 1-chloro-4-nitrobenzene.

Table 3. Reduction of 1-chloro-4-nitrobenzene using Catalyst (5 mg) in different reducing agents^a.

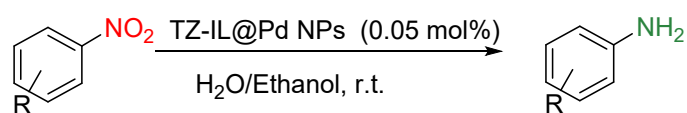


Entry	Reductant	Time (min)	Yield (%) ^b
1	Ammonium formate	60	4
2	Formic acid	60	7
3	Isopropyl alcohol	60	3
4	Hydrazine	60	5
5	Glycerol	60	6
6	Sodium borohydride	15	97


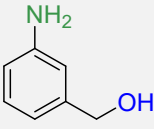
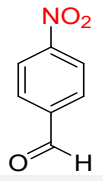
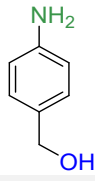
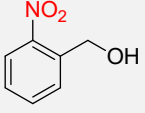
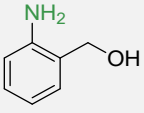
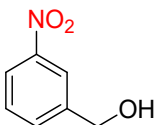
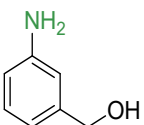
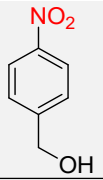
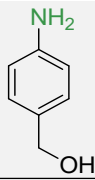
^a Reaction condition: 1-chloro-4-nitrobenzene (0.5 mmol), catalyst (12.5 mg, 0.05 mol% of Pd), H₂O/Ethanol (1:10, 1.5 mL), reducing (4 eq) at room temperature. ^b GC yields.

We used achieved optimized reaction conditions to reduce structurally different aromatic nitro compounds (Table 4). As can be seen in Table 4, reduction of aromatic nitro compounds having electron-donating groups such as -OMe, -Me, -OH, -NH₂ and aromatic nitro compounds having electron-withdrawing groups such as Cl, Br, -CHO, -COCH₃ as well as naphthalene and nitrobenzene proceed well and corresponding amines were obtained in high to excellent yields. It should be noted that reactions of aromatic nitro compounds having electron-withdrawing groups performed more efficiently than compounds having electron donating groups. Reduction of nitroarenes containing ortho-substituents performed well and desired products were obtained in 83-94% yields. In the case of nitro aromatics having a formyl group, both carbonyl and nitro groups were reduced to alcohol and amine, respectively and 71-79% were obtained under optimized reaction conditions (Table 4, entries 10-12). However, in these cases by doubling the amount of NaBH₄ yields were increased to 93-97% while halving the amount of NaBH₄, only 32-37% yields were obtained (Table 4, entries 10-12).

Table 4. catalyzed reductions of nitroarene derivatives ^{a,b}



Entry	Substrate	Product	Time(min)	Yield (%)
1			5	96
2			15	91
3			15	97
4			15	95
5			30	90
6			30	83
7			30	88
8			45	92
9			30	91
10			10	71%, 93 ^[c] , 32 ^[d]

11			10	75%, 97 ^[c] , 34 ^[d]
12			10	79%, 95 ^[c] , 37 ^[d]
13			10	94
14			10	96
15			10	97

^a Reaction condition: nitroarene (0.5 mmol), NaBH₄ (2 mmol), catalyst (12.5 mg, 0.05 mol% of Pd), H₂O (0.15 mL) and EtOH (1.35 mL)

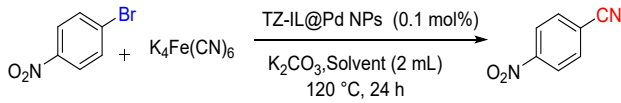
^b GC yields

^c Reaction proceeded using 4 mmol of NaBH₄

^d Reaction proceeded using 1 mmol of NaBH₄

In an attempt to extend the application of this catalyst, we turned to cyanation of aryl halides. For finding optimized reaction conditions, a reaction of 4-bromonitrobenzene was carried out with K₄Fe(CN)₆ and effects of solvent and base were studied (Tables 5, 6). Results showed that using 0.1 mol% of the catalyst, K₂CO₃ (0.75 mmol) as the base at 120 °C low yields were obtained in xylene, 1,4-dioxane, PEG-200, toluene, and DMSO (Table 5, entries 1-5) while 73% yield was achieved using DMF as a solvent (Table 5, entry 6).

Table 5. Reaction of 1-bromo-4-nitrobenzene with K₄Fe(CN)₆ in different Solvents ^{a,b}



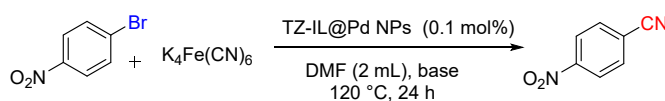
Entry	Solvent	Yield (%)
1	Xylene	<5
2	1,4-Dioxane	<5
3	PEG-200	<5

4	Toluene	<5
5	DMSO	DD
6	DMF	73

^a Reaction conditions: 1-bromo-4-nitrobenzene (0.5 mmol), K₄Fe(CN)₆ (0.3 mmol), K₂CO₃ (0.75 mmol), catalyst (25 mg, 0.1 mol% of Pd), 120 °C and solvent (2 mL). ^b GC yields

Selecting DMF as the solvent, we studied the effect of other bases such as Na₂CO₃, DABCO, Et₃N, KO^tBu, KOH, and NH₄OH (Table 6). Results of this study indicated that the highest reaction yield (88%) was obtained for Na₂CO₃ as a base (Table 6, entry 2), while lower yields were obtained for other bases.

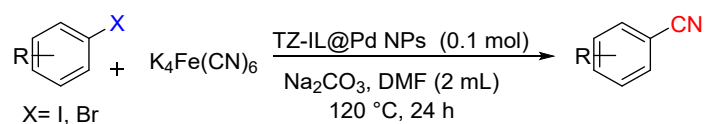
Table 6. Reaction of 1-bromo-4-nitrobenzene with K₄Fe(CN)₆ in different bases ^{a,b}



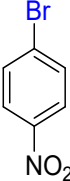
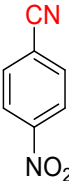
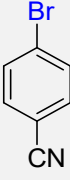
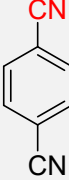
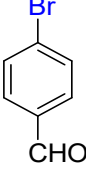
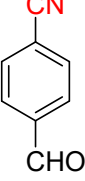
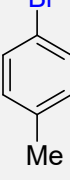
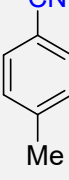
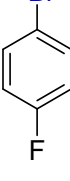
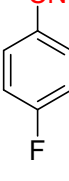
Entry	Base	Yield (%)
1	K ₂ CO ₃	73
2	Na ₂ CO ₃	88
3	DABCO	27
4	Et ₃ N	21
5	KO ^t Bu	18
6	KOH	31
7	NH ₄ OH	24

^a Reaction conditions: 1-bromo-4-nitrobenzene (0.5 mmol), K₄Fe(CN)₆ (0.3 mmol), base (0.75 mmol), catalyst (25 mg, 0.1 mol% of Pd), 120 °C and DMF (2 mL). ^b GC yields

Using optimized reaction conditions, cyanation of structurally different aryl bromides and iodides performed well and corresponding nitriles were produced in 71-90% yields (Table 7).

Table 7. Reaction of structurally different aryl iodides and bromides with $K_4Fe(CN)_6$ in the presence of catalyst ^{a,b}

Entry	Substrate	Product	Time(h)	Yield (%)
1			7	90
2			10	89
3			16	83
4			18	79
5			24	76
6			24	80
7			20	74

8			24	88
9			24	80
10			24	78
11			24	71
12			24	76

^a Reaction conditions: ArX (0.5 mmol), K₄FeCN₆ (0.3 mmol), Na₂CO₃ (0.75 mmol), catalyst (25 mg, 0.1 mol% of Pd), and DMF (2 mL). ^b GC using n-octane as an internal standard

The efficiency of the TZ-IL@Pd was compared with previously reported palladium catalyst in both cyanation of iodobenzene and reduction of nitrobenzene indicating the efficiency of the catalyst developed (Tables 8, 9).

Table 8. Comparison of results for the TZ-IL@Pd NPs catalyst with other catalysts for nitrobenzene reduction reaction.

Entry	Catalyst	Catalyst amount (mol%)	Temp (°C)	H ₂ Source	Time	Solvent	Yield (%)	Ref
1	Pd/C 5%	1	R.T	H ₃ PO ₂ (1 eq)- NaH ₂ PO ₂ (3 eq)	3h	H ₂ O-2-MeTHF	85	[70]
2	Fe ₃ O ₄ @PDA@POP@Pd-2.5%	20 mg-2.5 %	R.T	H ₂ balloon	1h	EtOH	100	[71]
3	PEG10k-Pd NPs	2	100	Hydrazine hydrate (8eq)	2h	-	90	[72]
4	polymeric PEG35k-Pd NPs	1.0	90	N ₂ H ₄ .H ₂ O (5 eq)	1.5h	-	100	[73]
5	Pd-gCN catalyst	5	70	N ₂ H ₄ .H ₂ O (1.2 eq)	4h	EtOH-reflux	99	[74]
6	PdNPs-PAAS	1	R.T	H ₂ balloon	3h	H ₂ O	99	[75]
7	TZ-IL@Pd NPs	0.05	R.T	NaBH ₄	0.08 h	H ₂ O:EtOH (1:9)	96	This work

Table 9. Comparison of results for the TZ-IL@Pd NPs catalyst with other catalysts for cyanation of iodobenzene.

Entry	Catalyst	Catalyst amount (mol%)	Temp (°C)	Time	Solvent	Yield (%)	Ref
1	Polymer-anchored Pd(II) Schiff base complex	0.5	110	18h	DMF	82	[76]
2	Pd NPs/RGO-Rosa canina	0.5	120	2h	DMF	96	[43]
3	Pd@PTPI-Me	0.3	120	10h	DMF	99	[77]
4	Fe ₃ O ₄ @PMDA/Pd	1.5	120	2h	DMF	96	[47]
5	Pd NPs/rGO-T. spicata	0.5	120	2h	DMF	96	[78]
6	GO/Fe ₃ O ₄ @PDA/Pd	1	120	2h	DMF	96	[40]
7	PSePd(II)jeanthra	1	100	18h	DMF	98	[79]
8	Pd-CD-PU-NS	1.7	120	15h	DMF:H ₂ O	70	[80]

Finally, we studied the recyclability of the catalyst for the reduction of 1-chloro-4-nitrobenzene and cyanation of iodobenzene under optimized reaction conditions. For this purpose, after completion of the reactions, the catalyst was separated by centrifugation and after washing with ethyl acetate and drying was used in another batch of the reaction. We found that catalyst was recyclable at least 5 times in cyanation and 10 times in reduction reactions with a small decrease in activity. Leaching study of Pd after 5 runs for cyanation and reduction reactions indicate 9 and 13% of Pd lose, respectively indicating high stability of the catalyst during the reactions (Fig. 6).

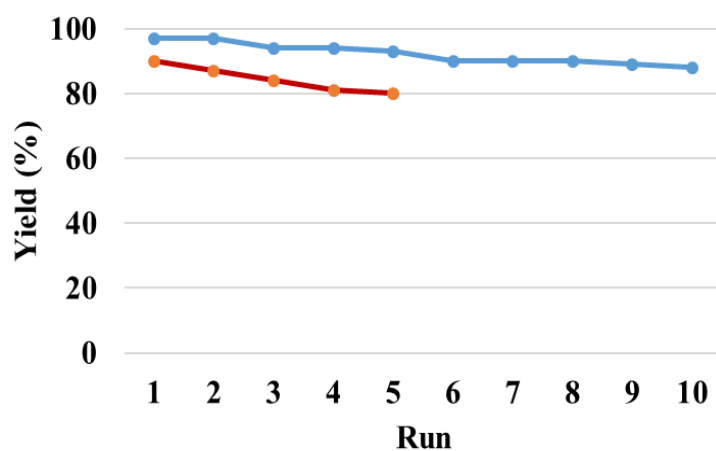


Fig. 6 Reusability of the catalyst for cyanation of iodobenzene (red) and reduction of 1-chloro-4-nitrobenzene (blue).

We also studied structure of the recycled catalyst in both cyanidation and reduction reactions using TEM images (Fig. 7, 8). Results showed that catalyst structure and uniform distribution of Pd nanoparticles were preserved.

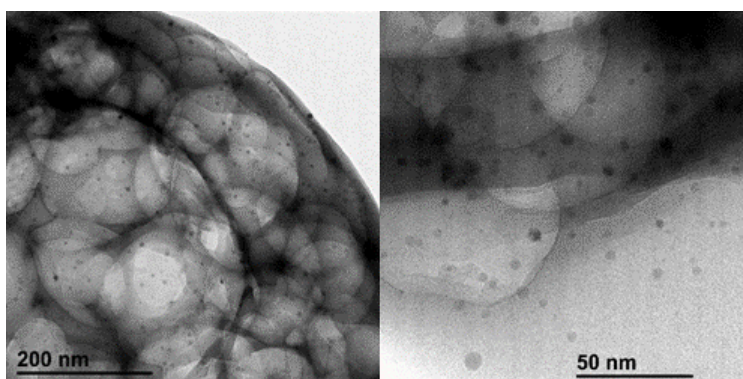


Fig. 7 TEM images and size distribution graph of reused catalyst in the reaction of iodobenzene with $K_4Fe(CN)_6$

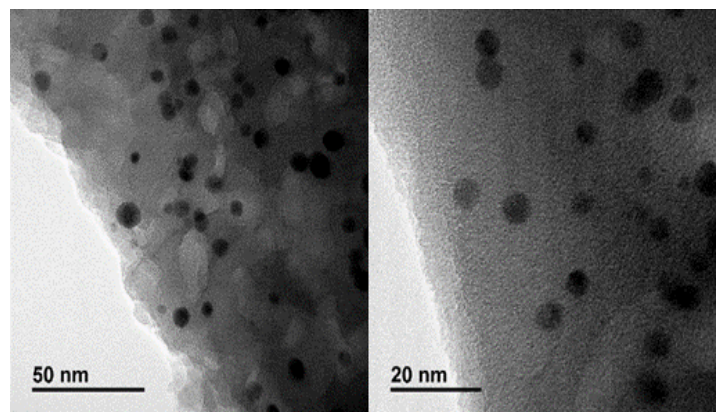


Fig. 8 TEM images and size distribution graph of reused catalyst in the reaction of iodobenzene with $K_4Fe(CN)_6$

4. Conclusions

In conclusion, a novel hyper branched nitrogen-rich polymer supported palladium nanoparticles was fabricated. The characterization results confirmed that palladium nanoparticles with an average size of 3-5 nanometers had been successfully incorporated into polymer. The polymer supported Pd NPs showed excellent catalytic performance in both reductions of nitro arenes and cyanation of aryl halides. This catalyst was recycled several times for both reactions and reused catalyst was characterized by TEM.

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