



# Metalloporphyrin supported on hyper cross-linked polymer: green protocol for reduction of nitroarenes

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## Abstract

In the current study, a Pd–porphyrin catalyst was anchored covalently onto functionalized polymeric spine based on a calix[4]resorcinarene. The achieved catalytic system was characterized, and its catalytic activity was investigated in the reduction of nitroarenes. The main advantages of the present work are: using water as green solvent, catalyst reusability, easy refinement of the products, excellent yields, and relatively short reaction times.

**Keywords** Metalloporphyrin · Calix[4]resorcinarene · Functionalized polymeric · Reduction of nitroarenes

## Introduction

The reduction of nitroarene is a common and simple way to produce amino-aromatics (AAs), which are versatile intermediates and precursors in the preparation of pharmaceuticals, pigments, dyes, agrochemicals, and polymers [1, 2]. The most typical way to generate aromatic amines is reduction of corresponding nitroarenes. One of the customary and interesting methods to reduce of the nitro group is catalytic transfer hydrogenation. Recently, noble metal nanoparticles are known for their modern applications in the field of catalysis, biotechnology, bio-engineering, and environmental remediation [3, 4]. Hence, the synthesis of noble metal nanoparticles and also their applications, particularly in catalysis, are of major interest for further studies, among which, palladium is the most effective catalyst in the surface hydrogenation reaction due to the simple availability of valence electrons. Therefore, many research groups have focused their interest on the expansion of efficient and active catalytic system. Porphyrins and metalloporphyrins are found widely in nature. They play important roles in the

basic mechanisms of vital organisms [5–8]. These systems have been extensively studied due to the catalytic application of organic synthesis, electrical light applications, and therapeutic properties. Although, they are known as homogeneous catalysts and their role can be highlighted by selectivity [9–11], their industrial applications have been limited due to the difficulty in the separation of catalysts from products. To take the advantages of both homogeneous and heterogeneous catalysts, immobilizing porphyrin onto high surface solids would be a powerful approach. A large number of materials were selected to be the supports of metal species in hydrogenation reactions, such as silica, zeolite, carbonaceous materials, metal oxides, and etc. Unlike the above compound, polymers are applicable and attractive support materials to synthesize of heterogeneous catalysts.

Today, porous organic polymers (POPs) with various potential applications attract a great deal of attention by incorporating porous properties with organic functionalization features. In this procedure, meso porous organic polymers (mesoPOP)s have been known incredibly, having to their structural pattern which equip suitable situations for immobilizing homogeneous catalysts and making them heterogenized [12, 13]. In fact, these extremely cross-linked amorphous polymers' porosity fortifies the catalytic activity of these materials by raising the number of accessible catalytic sites, increasing their concentration, adsorbing reactant molecules, and therewith growing the reaction rates. 3D-Network polymer based on calix[4]resorcinarene due to easy preparation and its unique properties, such as high thermal and chemical stability coupled with its susceptibility

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for various chemical modifications (acylation, alkylation, or silylation of hydroxyl groups and also nucleophilic substitution of the aromatic rings) under mild reaction conditions encouraged us to serve it. Under this light, as part of our continuing efforts to develop high performance and environmentally friendly procedures for various important reactions and transformations and according to our new interest in the application of the 3D-network porous polymer based on calix[4]resorcinarene for the preparation of biologically important molecules [14–21], herein, for the first time, we report the functionalization of polymeric calix[4]resorcinarene via a covalently anchored metalloporphyrin and the investigation of its efficiency as a heterogeneous catalyst for the synthesis of arylamines through the reduction of nitroarenes in water.

## Experimental

### Materials and methods

All the chemicals were purchased from Merck, Fluka and Aldrich companies. The progress of the reactions were monitored by TLC and the reported yields referred to isolated products. Products were characterized by comparison of their spectroscopic data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR) with those reported in the literature. The IR spectra were recorded on a Perkin Elmer Spectrum Version 10.4.4. FT-IR spectrophotometer via KBr pellets for the samples and catalyst in the range of 4000–400  $\text{cm}^{-1}$ . The SEM analyses were carried out using a LEO 1455VP scanning electron microscope, operating at 1–30 kV. The polymeric texture and its chemical composition was investigated using a Zeiss-EM10C transmission electron microscope (TEM) operated at 80 kV. Ultraviolet–Visible (UV–Vis) spectra were obtained from a Shimadzu UV-2600 UV–Vis spectrophotometer. Analyses for liquid samples were accomplished using a quartz cell with 1 cm path length.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker Advanced DPX 400 MHz spectrometer using TMS as internal standard. The heterogeneous catalysts were identified by X-ray powder diffraction (XRD) using a STOE diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 40 mA and amount of Pd in the prepared catalyst was specified by a Perkin-Elmer ICP analysis.

### Preparation of catalyst

#### Synthesis of calix[4]resorcinarene (1)

Calix[4]resorcinarene was made based on the already mentioned procedure [22, 23].

#### Synthesis of the 3D-network polymer based on calix[4]resorcinarene 2

In a round-bottomed flask, 42 mmol of formaldehyde was added to 14 mmol of the prepared calix[4]resorcinarene, and the mixture was dissolved in 40 mL NaOH solution (10%) at room temperature. The resulted mixture was heated to 90 °C and maintained at this temperature for 20 h. The surplus alkali was washed out from the resultant gel with cold water. Then, the gel was allowed to stand at 100 °C for 1 h. Then, the gel became acidic via treatment with the 0.1 M HCl solution. The produced solid was dried at 100 °C for 10 h [24].

#### Preparation of meso-tetrakis[4-(methoxycarbonyl)phenyl]porphyrin 3

Meso-tetrakis[4-(methoxycarbonyl)phenyl]porphyrin was made through modifying of A. D. Adler-F. R. Longo method [25]. Briefly, in a typical reaction, 2.33 mmol of freshly distilled pyrrole and 2.33 mmol of p-methoxycarbonylbenzaldehyde were added into 200 mL acetic acid. The mixture was refluxed for 4 h and cooled based on the room temperature. After cooling, the mixture was added to 100 mL methanol in an ice bath. The purple crystals were filtrated and washed with methanol and hot distilled water. Then, crude product was purified by column chromatography (silica gel, ethyl acetate /n-hexane = 20:1 as an eluent), and a desired purple solid of meso-tetrakis[4-(methoxycarbonyl)phenyl]porphyrin was obtained (37%).

#### Synthesis of Pd-porphyrin 4

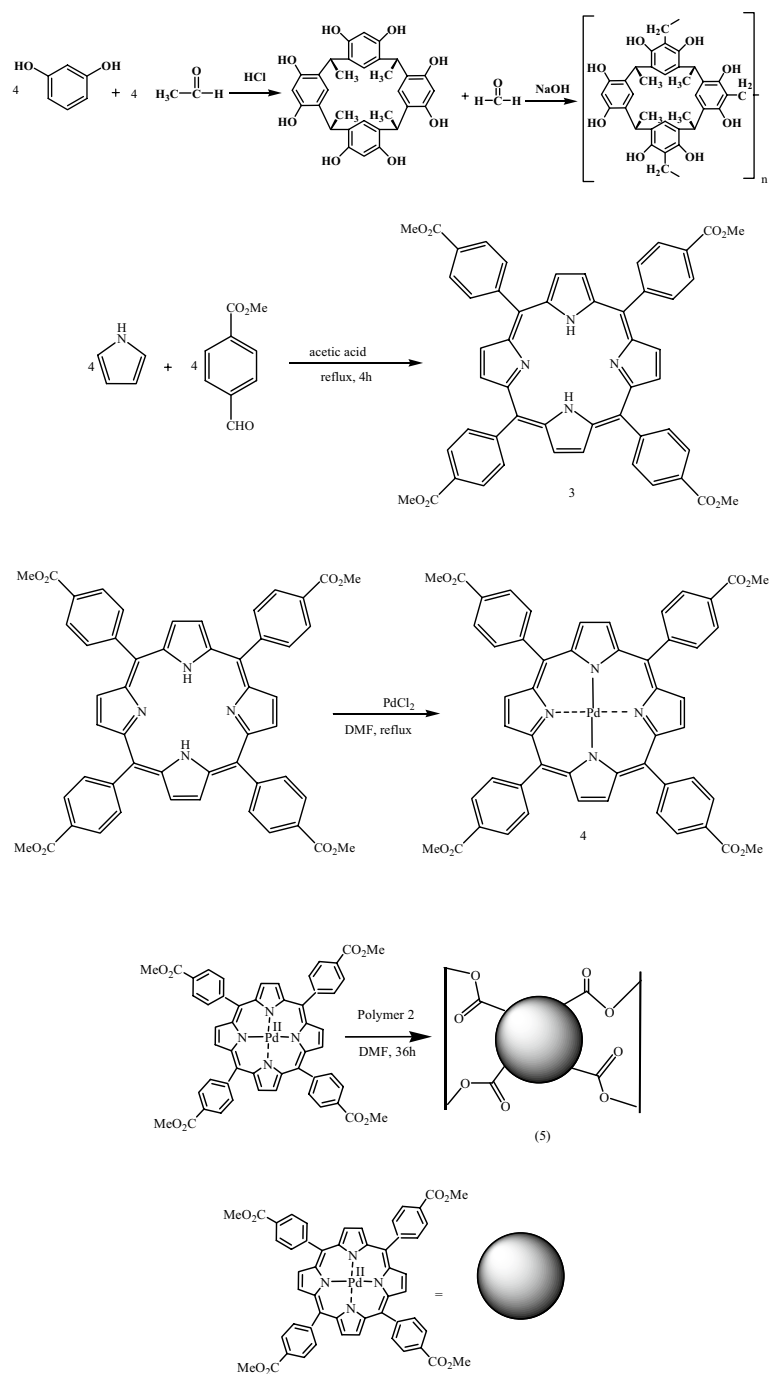
In a round-bottomed flask,  $\text{PdCl}_2$  (0.135 g) was added into a solution of meso-tetrakis[4-(methoxycarbonyl)phenyl]porphyrin ( $\text{H}_2\text{TMCPP}$ ) (0.3 g) in 100 mL of DMF and refluxed for 12 h. Then, Pd-TMCPP was purified by recrystallizing frequently and precipitating from DMF– $\text{H}_2\text{O}$  solutions [26].

#### Synthesis of Pd-porphyrin@polymer 5

According to the method reported by Fareghi-Alamdari, first, 5 gr of polymer(2) and 0.5 gr Pd-porphyrin[4] was added in 20 mL DMF after heating at 130 °C for 36 h. Then, the reaction mixture was cooled and filtered. Afterwards, it was washed exhaustively with DMF and deionized water. Finally, The produced catalyst was dried and stored under vacuum (Scheme 1) [27].

#### Typical method for the reduction of nitroarenes catalyzed by Pd-porphyrin@polymer

In a round bottom flask, nitrobenzene (1 mmol),  $\text{NaBH}_4$  (4 mmol), catalyst (15 mg), and water were added and

**Scheme 1** Schematic preparation of catalyst

heated at 55 °C, then, reacted for the required time. The completion of the reaction was monitored by TLC, using ethyl acetate/ *n*-hexane (1:10) as eluent. After the finalization of the reaction, the Pd-porphyrin@polymer was separated from the reaction mixture by filtration. Then, the product was extracted from the liquid with  $\text{Et}_2\text{O}$  and purified by column chromatography using *n*-hexane/ ethyl acetate as solvent to obtain the pure compound.

## Results and discussion

Growing interest in applying heterogeneous catalysis for developing useful and green synthetic methodologies in chemical transformations, prompted us to report an efficient, convenient, and practical procedure for synthesizing a series of aromatic amines using the new developed

metalloporphyrin immobilized on network polymer based on calix[4]resorcinarene as an eco-friendly solid supported catalyst with high catalytic activity under mild conditions. Scheme 1 shows the synthetic strategy for the mentioned catalyst preparation. To achieve this purpose, first, the 3D-network polymer 2 was prepared via the reaction of resorcinol and acetaldehyde, followed by the polycondensation of calix[4]resorcinarene 1 with formaldehyde [22, 24] as outlined in Scheme 1. The formation of compounds 1 and 2 was confirmed through a series of spectroscopic analysis (available in the ESI) [14]. In the second step, the porphyrin ligand was synthesized based on the results of the previous reports [25]. Then, the porphyrin ligand was metalated [26] (compound 4). Subsequently, metalloporphyrin immobilized on polymer 2 was produced as a result of the reaction between compound 2 and compound 4 (Scheme 1). To verify the covalent interactions between metalloporphyrin and polymer in metalloporphyrin@polymer, FTIR spectra were recorded (Fig. 1). As shown in Fig. 1a, d different IR spectra were observed for porphyrin and Pd-porphyrin complex. Moreover, the results indicated the stretching and bending frequencies of the N–H bond related to free base porphyrin placed at  $\sim 3310$  and  $960\text{ cm}^{-1}$ . However, the palladium ion was entered into the porphyrin ring, the N–H bond vibration frequency of porphyrin ligand was vanished, and the functional groups of Pd–N bond were established at  $\sim 1000\text{ cm}^{-1}$ , which resulted in forming Pd–porphyrin complex [28]. Additionally, the bands as  $1722$  and  $1604\text{ cm}^{-1}$  were assigned to carbonyl of ester and C=N, respectively. In addition, a broad band at  $3200\text{--}3600\text{ cm}^{-1}$  revealed that all phenolic

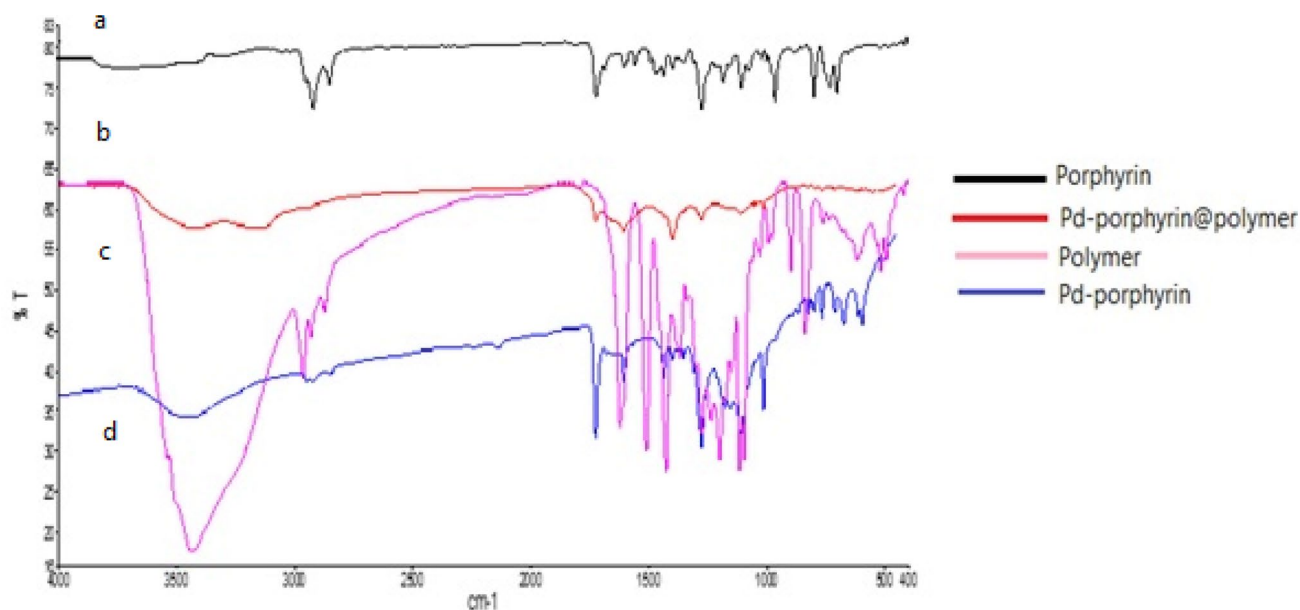
hydroxyl groups of polymer 2 were not completely functionalized due to steric hindrance (compared with the IR spectrum of polymer 2 in the ESI<sup>†</sup>). So, the FTIR data qualitatively confirmed the successful grafting of Pd–porphyrin onto the polymer surface.

In addition to FTIR spectrum, other techniques were considered for better catalyst verification (UV–VIS, SEM, XRD, and EDS). Furthermore, UV–Vis spectroscopy was also used to evaluate the Pd–porphyrin@polymer. As shown in Fig. 2, the absorptions peaks at 417, 525, 560, 600, and 658 nm relayed on H<sub>2</sub>TMCPP, whereas the sample gives new absorption peaks at 413, 535, and 580 nm after metalation with the palladium cation (solvent: CHCl<sub>3</sub>).

The morphology and size of the Pd–porphyrin@polymer were observed by scanning electron microscopy (SEM). The image shows that the Pd–porphyrin is placed on the polymer (Fig. 3a). The energy dispersive spectroscopy (EDS) analysis was used to determine the Pd–porphyrin@polymer, confirming the presence of nitrogen and palladium in the mentioned catalyst evaluate (Fig. 3b).

The TEM image of the fresh and used catalyst after 5th runs was provided to study the feasible deactivation mechanism of the Pd–porphyrin@Polymer catalysts following the recycling tests. The comparison among TEM images of primary catalyst and reused Pd–porphyrin@polymer (Fig. 4) displayed slight degree of agglomeration of in reused catalyst. This result shows that the mechanism of deactivation is likely to involve the formation of agglomerated Pd black.

The wide-angle X-ray diffraction was conducted to trace the crystalline structure and size of the supported Pd.



**Fig. 1** FT-IR spectra of **a** synthesized porphyrin, **b** Pd-porphyrin@polymer, **c** polymer, **d** Pd-porphyrin complex

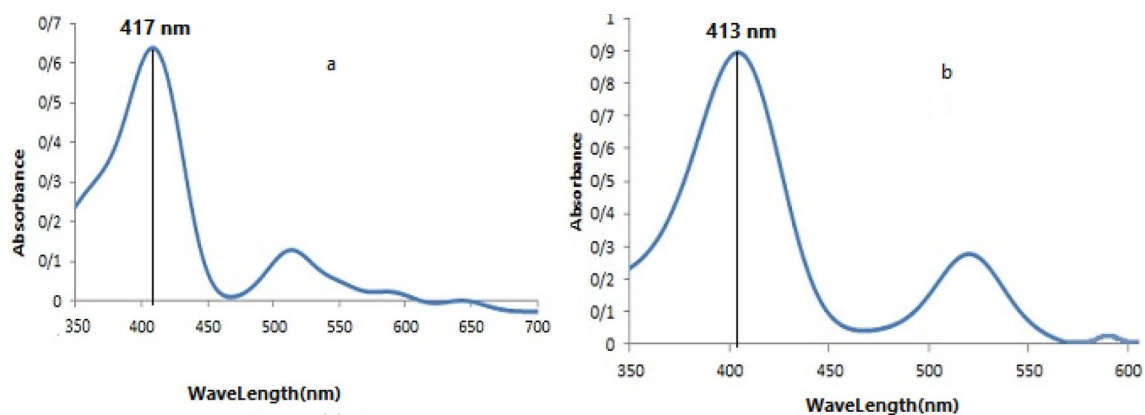


Fig. 2 UV-Vis spectra of Porphyrin (a) and Pd-porphyrin@polymer (b)

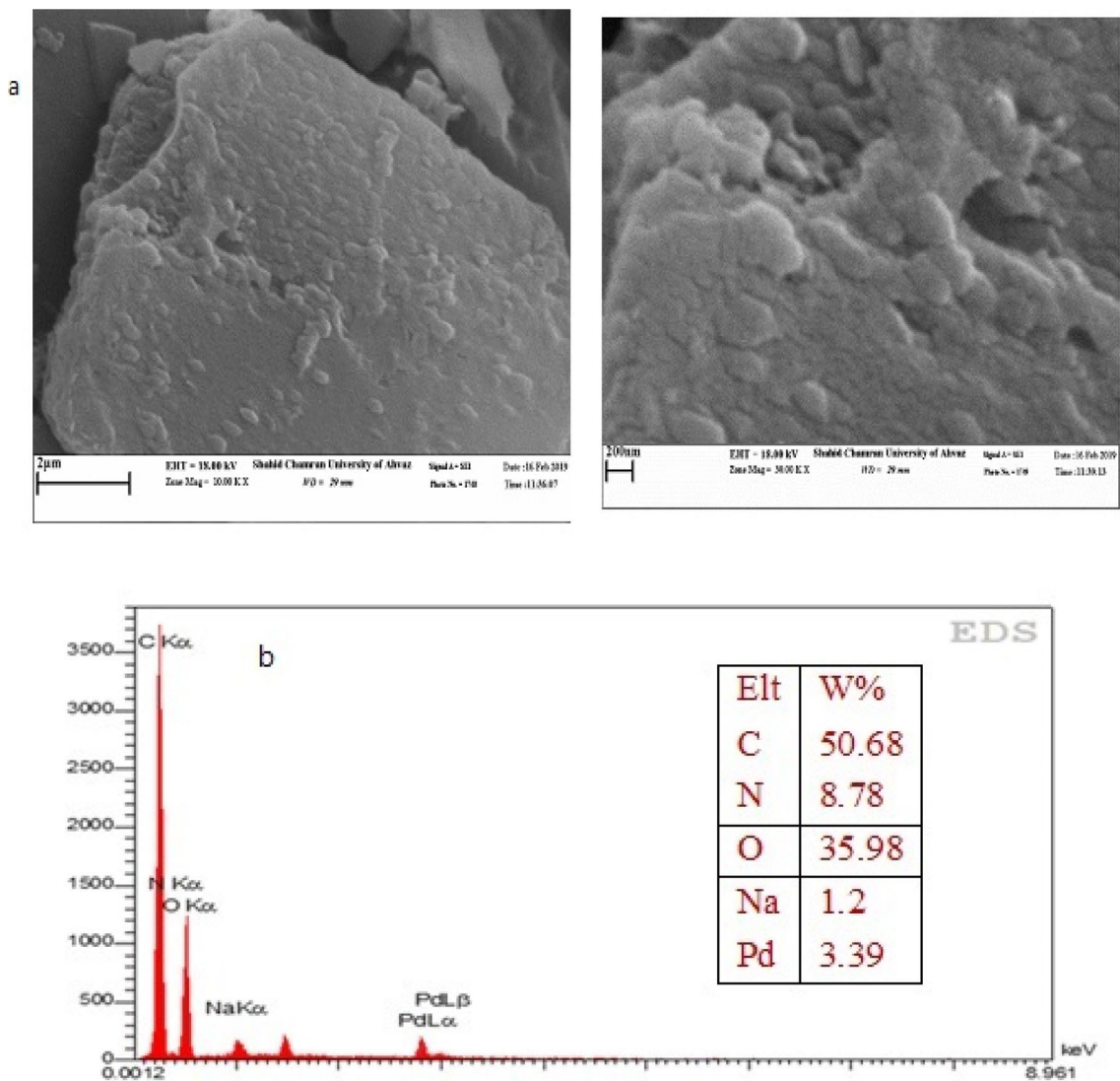
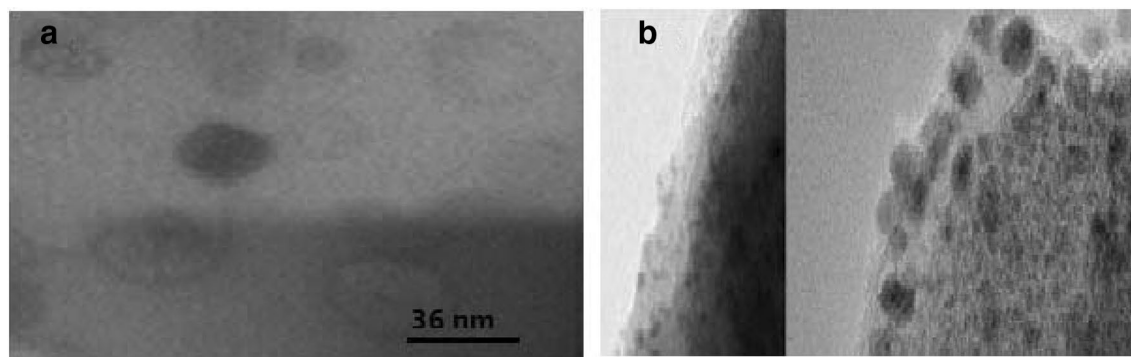
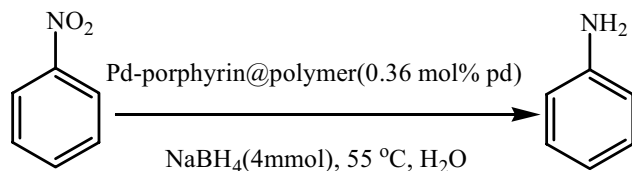
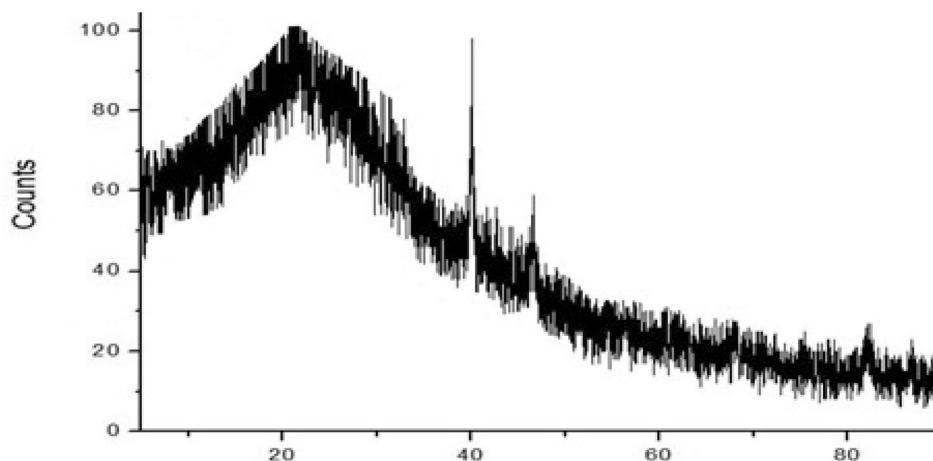


Fig. 3 SEM images of catalyst (a) and EDS spectrum of catalyst (b)



**Fig. 4** TEM images of **a** fresh and **b** reused catalysts

**Fig. 5** XRD pattern of catalyst



**Scheme 2** Schematic reduction of nitrobenzene

Figure 5 depicts that four prominent peaks at  $2\theta$  values of about  $40^\circ$ ,  $46^\circ$ ,  $68^\circ$ , and  $81^\circ$  corresponding to the characteristic of crystalline Pd. (111), (200), (220), and (311) confirmed the success of Pd ions' reduction [29].

After the catalyst verification, we examined the catalytic activity and application of Pd-porphyrin@polymer in the aqueous reduction of nitroarenes in the presence of  $\text{NaBH}_4$ . The reduction of nitrobenzene was selected as a model compound over Pd-porphyrin@polymer catalyst to optimize the reaction conditions (Scheme 2). We studied various conditions, including solvents, molar ratio of hydrogen source, temperature, and amount of catalyst, the results of which are summarized in Table 1. Match up with Table 1, the best

**Table 1** Optimization of the reaction conditions for the reduction of nitrobenzene

Entry	Catalyst(mg)	Solvent	$\text{NaBH}_4$	T ( $^\circ\text{C}$ )	Yield (%)
1	–	$\text{H}_2\text{O}$	2	55	Trace
2	10	$\text{H}_2\text{O}$	2	55	78
3	10	$\text{H}_2\text{O}$	4	55	90
4	15	$\text{H}_2\text{O}$	4	55	98
5	20	$\text{H}_2\text{O}$	4	55	95
5	15	DMF	4	55	70
6	15	Toluene	4	55	30
7	15	EtOH	4	55	75
8	15	$\text{H}_2\text{O}$ -EtOH	4	55	77
9	15	$\text{H}_2\text{O}$	4	25	80
10	15	$\text{H}_2\text{O}$	4	100	88

Reaction conditions: nitrobenzene (1 mmol), solvent (6 ml)

yield and the shortest time for this catalytic system were observed in the presence of 15 mg catalyst which is equal to 0.36 mol% of Pd, 4 mmol of  $\text{NaBH}_4$  in water at  $55^\circ\text{C}$  for 1 mmol of nitrobenzene. To verify the catalyst efficiency,

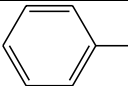
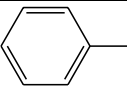
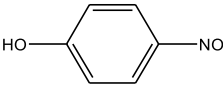
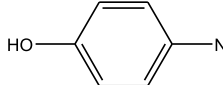

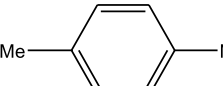
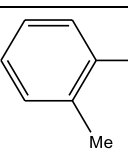
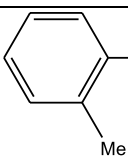
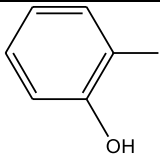
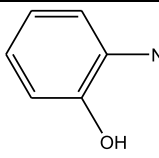
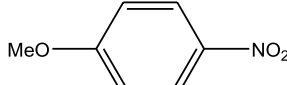

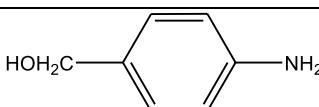
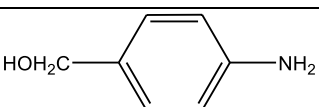
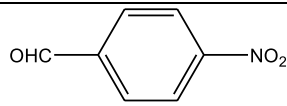
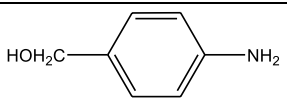
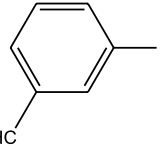
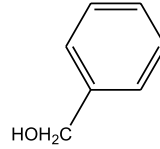
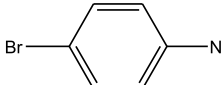
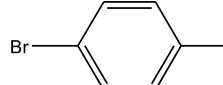
the model compound was probed in the absence of catalyst. In this case, only a trace amount of product was detected (Table 1, entry 1).

To determine the catalytic activity of Pd-porphyrin@polymer, a wide variety of nitroarenes compounds were investigated. As displayed in Table 2 that either electron withdrawing or electron donating substituents in all positions of the phenyl ring (ortho, meta, or para) participated

well in this reaction to give the corresponding products in high to excellent yields. Also, in entries (8, 9), both nitro and aldehyde functional groups were reduced by the present protocol.

A brief comparison between the efficiency of the present catalyst and some of those catalysts reported in the literature is listed in Table 3. It is clearly displayed that the presented methodology in this paper is superior to the

**Table 2** Reduction of nitroarenes using milder reducing sources

Entry	Substrate	Product	Time (min)	Yield%
1			10	98
2			20	90
3			20	91
4			25	89
5			25	94
6			20	95
7			25	94
8			25	90
9			30	85
10			35	95

Reaction conditions: nitroarenes (1 mmol), catalyst (15 mg), NaBH<sub>4</sub> (4 mmol), and H<sub>2</sub>O (6 mL) at 55 °C

**Table 3** Comparison of catalytic activity of Pd-porphyrin@polymer with other heterogeneous catalysts for the reduction of nitrobenzene

Entry	Catalyst	Reaction conditions	Yield (%)	Reference
1	Ni-MoO <sub>3</sub> /CN@SBA-15 (20 mg)	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, EtOH, 40 °C, 30 min	99	[30]
2	Graphene-Fe <sub>3</sub> O <sub>4</sub> (0.01 g)	N <sub>2</sub> H <sub>4</sub> , H <sub>2</sub> O, 70 °C, 20 min	88	[31]
3	Polymer supported Pd NPs (0.04 g)	NaBH <sub>4</sub> , H <sub>2</sub> O, rt, 6 h	96	[32]
4	Carbon nitride supported Pd NPs (5 mol%)	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, EtOH, reflux, 4 h	99	[33]
5	Scrap automobile catalyst (0.3 g)	NaBH <sub>4</sub> , EtOH/H <sub>2</sub> O, 50 °C, 4 h	95	[34]
6	Co-Co <sub>2</sub> B nanocomposites (0.02 g)	NaBH <sub>4</sub> , H <sub>2</sub> O, rt, 15 min	64	[35]
7	Pd-porphyrin@polymer (0.015gr)	NaBH <sub>4</sub> , H <sub>2</sub> O, 55 °C, 10 min	98	This work

rt room temperature, NP nanoparticle

**Table 4** Recyclability of catalyst on the reduction of nitrobenzene

Run no.	1	2	3	4	5
Yield %	98	95	95	90	88
Reaction conditions: nitrobenzene (1 mmol), catalyst (15 mg), NaBH <sub>4</sub> (4 mmol), and H <sub>2</sub> O (6 mL) at 55 °C					

most of the previously reported methods in terms of catalyst amount, reaction time or product yield.

The catalyst reusability was also examined for the model reaction under optimum conditions. Upon the completion of the reaction, the catalyst was recycled via simple filtration, washed with methanol and water, dried, and reused for five another successive runs without remarkable loss in activity. The results are displayed in Table 4. Furthermore, its amount in the product was determined by ICP-OES, and no leaching of palladium was discovered.

## Conclusion

In summary, we successfully proposed a new type of Pd-porphyrin modified organic polymer-based catalyst combining the catalytic power of transition metal complexes with the architecture of 3D-network polymer and shows particularly high efficiency for the reduction of nitroarenes. Water as a green solvent, catalyst reusability, high product yields, short reaction times, relatively mild reaction conditions, and simple work-up are possibly the most favorable advantages of the reported method. The described catalytic system provides a highly promising material through coupling the advantages of homogeneous and heterogeneous catalysts to be applied extensively in different aspects of science, industry, and technology.

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