

Synthesis of Dendrimer Assisted Co-Pd Bimetallic Nanoparticles and Catalytic Activity for Suzuki–Miyaura Coupling Reactions

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Abstract: Triazine-based dendrimer 2,4,6-tris(di-acetamido)-1,3,5-triazine encapsulated heterogeneous Co-Pd bimetallic nanoparticles (NPS) were prepared through sequential loading method from the dendrimer which was synthesized directly between the reaction of 2,4,6-triamino-1,3,5-triazine and acetyl chloride at room temperature about 2 hours. The physicochemical characteristics of Co-Pd bimetallic NPS were studied with the aid of EDX, XRD, TG& DSC techniques. The presence of cobalt was 55.75% and palladium was 9.40% of the mass of the 2,4,6-tris(di-acetamido)-1,3,5-triazine assisted Co-Pd Bimetallic NPs 4 observed from EDX analysis. The TG& DSC analysis curves indicated the thermal stability up to 320°C which is a very important steadiness key for catalytic effectiveness of the prepared Co-Pd Bimetallic NPs 4. The nano-shape FCC structure of Co-Pd bimetallic NPs was confirmed by XRD analysis. The average size of Co-Pd bimetallic NPs of 17.50 nm length was calculated through the Debye-Scherrer formula while TEM analysis showed the average particle size was 14.50 nm. The dendrimer was also analyzed by IR, ¹HNMR, ¹³CNMR and elemental analysis. The catalytic performance of these nanoparticles' catalyst was explored for C–C coupling reactions such as Suzuki–Miyaura at moderate reaction conditions whereas the reusing potential of the catalyst was evaluated without noticeable loss of activity for five successive runs. All the results of the analysis of this catalyst make it a cost-effective and highly active catalyst for the carbon-carbon cross-coupling reactions which are demand in chemical and pharmaceutical industries.

Keywords: Bimetallic Nanoparticles (NPs), Triazine, Dendrimer and Suzuki–Miyaura Reaction

1. Introduction

Catalytic C-C bond forming reactions provide all reactive synthetic routes to a variety of important chemicals and pharmaceuticals of their building blocks. The advent of nanotechnology for the production of metal nanoparticles opens up new possibilities for a possible revolution in the field of catalysis. Dendrimers are highly branched macromolecules and are generally described as a spherical structure with a high degree of symmetry [1-2]. Dendrimers are also considered to have new types of hosts for containing guest molecules due to their three-dimensional structure with the internal cavity receiving space, so many metal nanoparticles have been successfully synthesized using

dendrimer as a template [3-5]. The driving force for encapsulation within host dendrimer may be based on electrostatic interactions, complexation reactions, steric confinement, various types of weak forces (van der Waals, hydrogen bonding, hydrophobic force, etc.) and their combinations [6-7].

As a result the preparation technique for monometallic or bimetallic nanoparticles via dendrimer templates [8-9] has at least five potential benefits: (i) with relatively uniform composition and structure; dendrimer patterns themselves afford distinct nanoparticle replicas; (ii) nanoparticles area unit stabilized by encapsulation in dendrimers and thus don't agglomerate throughout catalytic reactions; (iii) the nanoparticles are mainly retained in the dendrimers by steric effects, and therefore, a substantial portion of their surface is

not passivated and available for participation in catalytic reactions; (iv) the dendrimer branches can be used as selective gates to control the access of molecules (substrates) to the encapsulated (catalytic) nanoparticles; and (v) the dendrimer periphery can be tailored to control the solubility of the hybrid nanocomposite and to be used as a handle to facilitate linkage with surfaces and other polymers. However, bimetallic dendrimer-encapsulated nanoparticles have been receiving a significant amount of attention due to their promising properties, unique characteristics and novel applications in catalysis and other advanced nano-science and technology areas [10]. Bimetallic nanoparticles based on Pt, Pd, or Rh is that 3d transition metals are abundant, and low priced, and can be acclimated to alter big-ticket blue-blooded metals in catalytic processes [11-12]. Nano cobalt supported nanopalladium catalyst obtained by an innovative methodology of nanoparticle transfer from the intermediate carrier metallodendrimer to the target metallic element carrier was an extremely economical and selective catalyst, giving the maximum amount as quantitative conversion and yield during a series of Suzuki-Miyaura reaction, Sonogashira reaction [13]. Indeed, catalysts for bimetallic nanoparticles incorporated in/on insoluble endorses with ligand-free and marginal or no leaching are essential from the point of view of both reducing environmental burdens and value-efficiency. Constitutional simplicity, standardized diffusion, reduced cost and dependable dendrimeric surface, improved efficiency and life cycle remain the significant challenges for a heterogeneous catalyst.

Moreover, to the best of our ability, no research can be acquired in the literature on the synthesis of melamine-based dendrimer embedded bimetallic Co-Pd NPs including the use of their heterogeneous catalytic activity in Suzuki-Miyaura cross-coupling reactions. Here, we have reported the synthesis, characterization, and utilization as a catalyst bimetallic Co-Pd NPs.

2. Experimental

2.1. Materials and Methods

All reagents such as 2,4,6-triamino-1,3,5-triazine, acetyl chloride, phenylboronic acid, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and PdCl_2 as well as all solvents such as DMF, DMSO, CH_3CN , $\text{C}_2\text{H}_5\text{OH}$, DMF, and bases such as NaOH, KOH, KO^tBu , Na_2CO_3 , and Et_3N , were purchased from Aldrich and used directly. The IR spectrum was taken with KBr pellets on a Shimadzu FTIR 8400S Fourier Transform. On the BRUKER DPX-400 spectrophotometer, NMR spectra were taken using tetramethylsilane as an internal standard. The chromatography of the analytical thin layer (TLC) was silica gel, 60 F 254 coated on 25 sheets of aluminum TCC (20 / 20 cm). On silica gel 60 N (neutral, 40-100 μM) silica gel column chromatographic separations were made. The thermal stability of nanoparticles was ascertained by a thermogravimetric analyzer (NETZSCH STA 449F3) from 26 to 600°C. TG and DSC data were detected in a nitrogen atmosphere using crisp aluminum oxide at 10 °k / min

heating rates and 40 and 60 mL/min flow rates. SEM and EDX of Co-Pd bimetallic NPs 4 were taken by the JEOL-JSM-7600F. A PANANALYTICAL X-ray diffractometer was also used to define particle size and phase. TEM analysis was accomplished by Philips CM12 transmission electron microscope (operating at 200 KeV).

2.2. Synthesis of Dendrimer 3 and Dendrimer 3 Assisted Co-Pd bimetallic Nanoparticles 4

2.2.1. Synthesis of 2,4,6-tris(di-acetamido)-1,3,5-triazine (Dendrimer 3)

The mixture of 0.3 g (0.00237 mol) 2,4,6-triamino-1,3,5-triazine, 4 mL of acetyl chloride was added to 8 mL of DMSO and the reaction mixture was stirred in a 250 mL round bottom flask at room temperature for about 2 hours. The reaction was observed by TLC. The reaction was stopped by introducing distilled water after the perfect transformation of the reactants into products. The reaction combination with CHCl_3 was then retrieved. After the solvent was removed, the product was crystallized using ethanol and the required compound 3 was found as white crystalline solid, m. p. 137-139°C, White crystalline solid; yield: 95%, IR (KBr): ν_{max} 3035, 2965, 1687, 1675, 1620, 1530, 1360 and 1290 cm^{-1} . ^1H NMR (400 MHz, D_2O): 2.40 (s, 18H) ppm. ^{13}C NMR (100 MHz, D_2O): 66.83, 88.34, 97.34, 151.83 and 161.44 ppm. Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_5\text{O}_6$; C 47.62, H 4.80, N 22.21; found: C 47.58, H 4.78, N 22.15

2.2.2. Synthesis of 2,4,6-tris(di-acetamido)-1,3,5-triazine, 3 Assisted Co-Pd Bimetallic NPs 4

In CH_3CN (12 mL), 0.200 g 2,4,6-tris(di-acetamido)-1,3,5-triazine 3 (0.00054 mmol), 0.00096 g PdCl_2 , $\text{NH}_2\text{-NH}_2 \cdot \text{H}_2\text{O}$ (1.5 mmol) were stirred for 1 hour under reflux in a round bottom flask at 80°C. Then 0.01536 g of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_2\text{-NH}_2 \cdot \text{H}_2\text{O}$ were added to the reaction mixture dropwise to a certain extent exceeding the equivalent amount of copper salt. In order to maintain pH 11, the NaOH solution (0.3 M) was gradually added to the reaction mixture and the suspension was stirred with a magnetic stirring bar at 80°C for 2 hours. After the reaction mixture had been settled, the black residue originated. The residue was filtered after the reaction mixture was centrifuged (4000 rpm for 20 min), washed with distilled water and acetone and dried overnight at 120°C in an oven.

2.3. Application of 2,4,6-tris(di-acetamido)-1,3,5-triazine, 3 Assisted Co-Pd Bimetallic NPs 4 in the Suzuki-Miyaura Coupling Reactions

Co-Pd bimetallic NPs 4 (1.0 mol%), aryl halides (1.0 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (1 mmol), and 5 mL of $\text{EtOH}/\text{H}_2\text{O}$ (1:4 v/v) were stirred about 1h at 70°C to a round bottom flask. With the aid of TLC chromatography, the reaction was monitored and after completing the reaction, the solvent was removed through vacuum rotary evaporator. The residue was extracted with CHCl_3 as well as purified by column chromatography using ethyl acetate/hexane (1:5 v/v).

2.3.1. Synthesis of Biphenyl 11

pale yellowish, yield %, (table 2), solid, mp. 66-68°C (lit. 69.2°C) [14]

IR (KBr): ν_{\max} 3017.71, 1597.65, 1483.53, 1435.52, 1308.43, 1217.27, 977.13, 800.65

^1H NMR (400 MHz, CDCl_3): δ 7.63 (dd, $J=7.2$ Hz, 1.6 Hz, 2H), 7.54 (t, $J=7.2$ Hz, 4H), 7.34 (dd, $J=5.6$ Hz, 1.2 Hz, 4H), ^{13}C NMR (100 MHz, CDCl_3): δ 141.30, 128.55, 127.78, 127.26.

2.3.2. Synthesis of 4-Methyl-biphenyl 12

white crystalline solid, yield %, (table 2), mp. 44-46°C (lit. 44-47°C) [14]

IR (KBr): ν_{\max} 2922.24, 1488.40, 1445.10, 1403.50, 1378.54, 1216.65, 823.43, 755.67

^1H NMR (400 MHz, CDCl_3): δ 2.28 (s, 3H), 7.25 (d, $J=8.4$ Hz, 2H), 7.31-7.34 (m, 1H), 7.35-7.44 (m, 2H), 7.58 (d, $J=8.0$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.60, 127.25, 127.95, 128.10, 129.20, 137.60, 138.00, 141.90

2.3.3. Synthesis of 4-Methoxy-biphenyl 13

white crystalline solid, yield %, (table 2), mp. 83-85°C (lit. 86-90°C) [14]

IR (KBr): ν_{\max} 3020.65, 1613.63, 1605.65, 1519.92, 1487.52, 1216.65, 909.13, 759.65

^1H NMR (400 MHz, CDCl_3): δ 6.81 (d, $J=7.2$ Hz, 3H), 7.49 (t, $J=7.2$ Hz, 1H), 7.54 (t, $J=7.2$ Hz, 2H), 7.57-7.70 (m, 4H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 55.21, 114.11, 126.20, 126.40, 128.20, 128.40, 133.21, 140.61, 159.22.

3. Result and Discussions

3.1. Synthesis and Characterization

Dendrimer 3 was produced by a reaction of 0.3 g (0.00237 mol) 2,4,6-triamino-1,3,5-triazine 1 with 4 mL of acetyl chloride in anhydrous DMSO for 2 hours in a nitrogen atmosphere at room temperature (Figure 4). The growth of the reaction was monitored by thin layer chromatography (TLC) and the solid reaction mixture was washed with sodium bicarbonate solution after completion of the reaction and recrystallized with ethanol which gave the dendrimerized product 3. The product was analyzed by using IR, ^1H NMR, ^{13}C NMR (Figures 1-3).

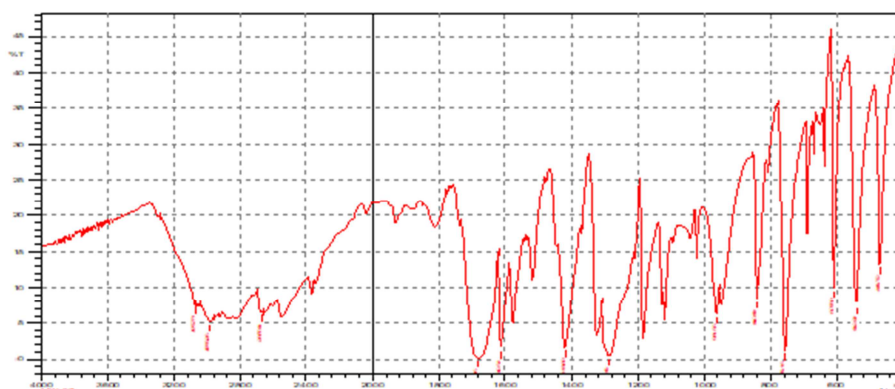


Figure 1. IR of 2,4,6-tris(di-acetamido)-1,3,5-triazine 3.

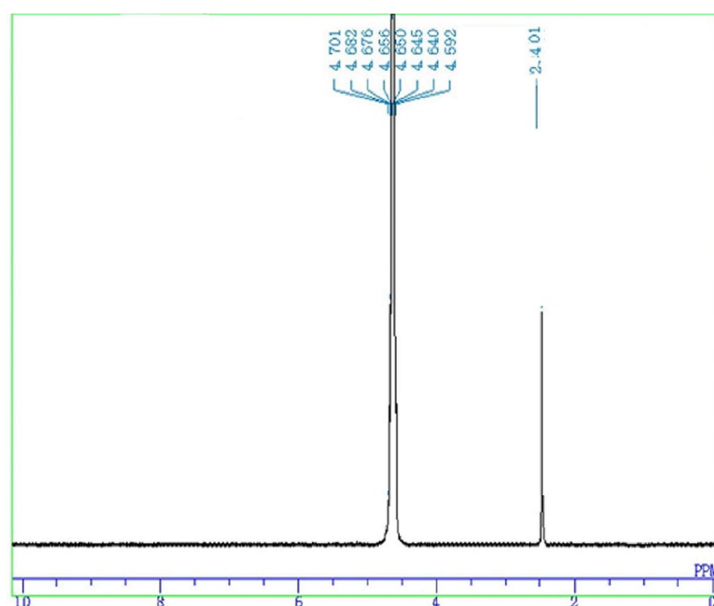


Figure 2. ^1H NMR of 2,4,6-tris(di-acetamido)-1,3,5-triazine 3.

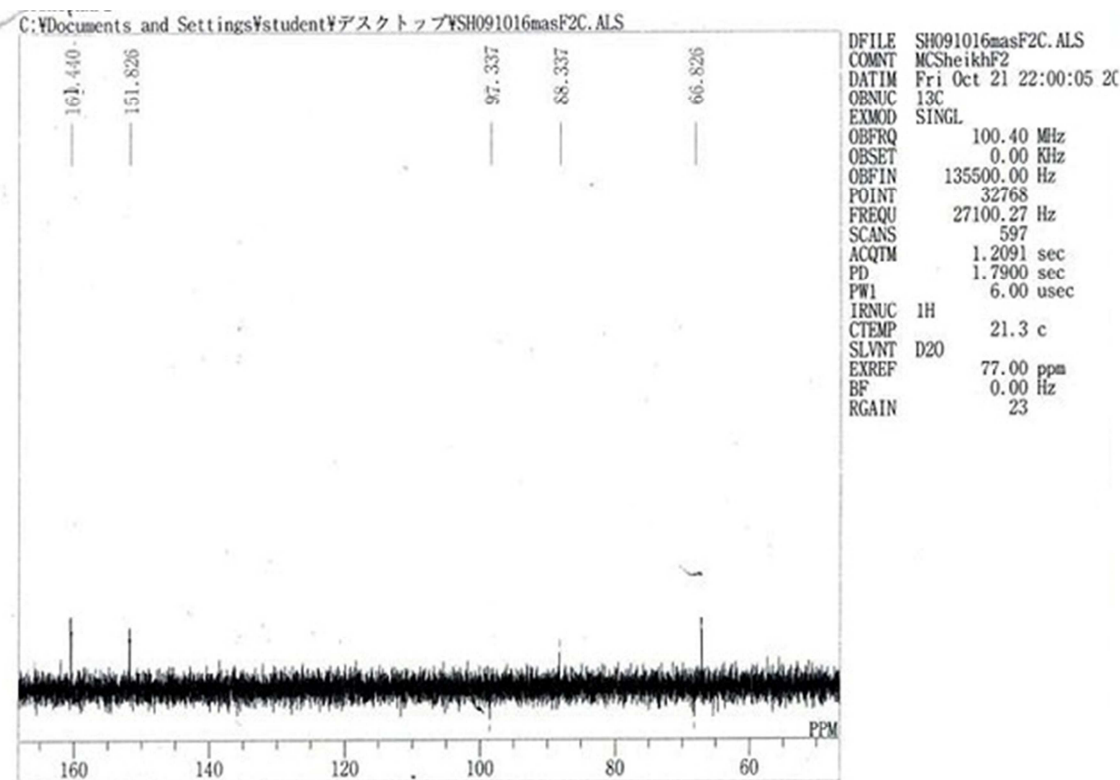


Figure 3. ^{13}C NMR of 2,4,6-tris(di-acetamido)-1,3,5-triazine 3.

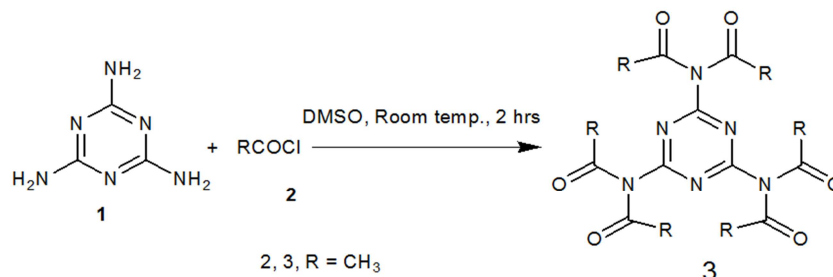


Figure 4. Synthesis of 2,4,6-tris(di-acetamido)-1,3,5-triazine 3.

The presence of essential peaks in the IR spectrum revealed compound 3's structure. The peak at the 3035, 2965, and 1530 cm^{-1} stretching bands suggested the existence of aromatic C-H, aliphatic C-H and aromatic C=C respectively, while the C=O group was ensured by the peak at 1620–1780 cm^{-1} . Indeed it is remarkable that there is no band for N-H

close to 3400–3200 cm^{-1} which has been shown to have changed 1° amino group of triazine into 3° amido group. The preferred dendrimer 3 was also afforded in ^1H NMR and ^{13}C NMR spectra. There is no NH or NH₂ group in the ^1H NMR peak, which further defined the structure of 3. The structure of compound 3 was also confirmed by the elemental analysis.

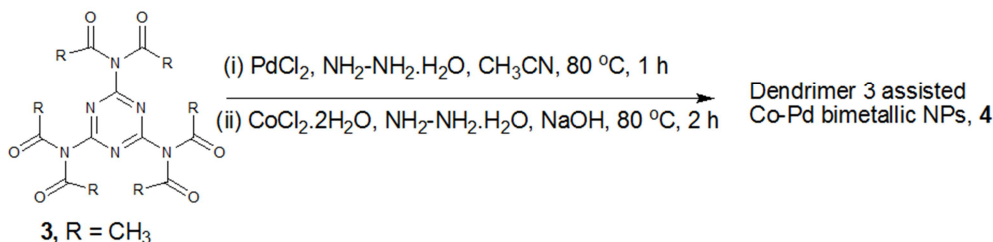


Figure 5. Synthesis of 2,4,6-tris(di-acetamido)-1,3,5-triazine assisted bimetallic Co-Pd NPs 4.

A sequential loading approach (Figure 5) was used to produce the triazine-based dendrimer 3 assisted bimetallic Co-Pd NPs 4 and thus characterized by various physicochemical methods such as EDX, XRD, TGA, and DSC. The existence of cobalt was 55.75% and palladium 9.40% of the mass of the synthesized NPs 4 (Figure 6) was found by EDX analysis.

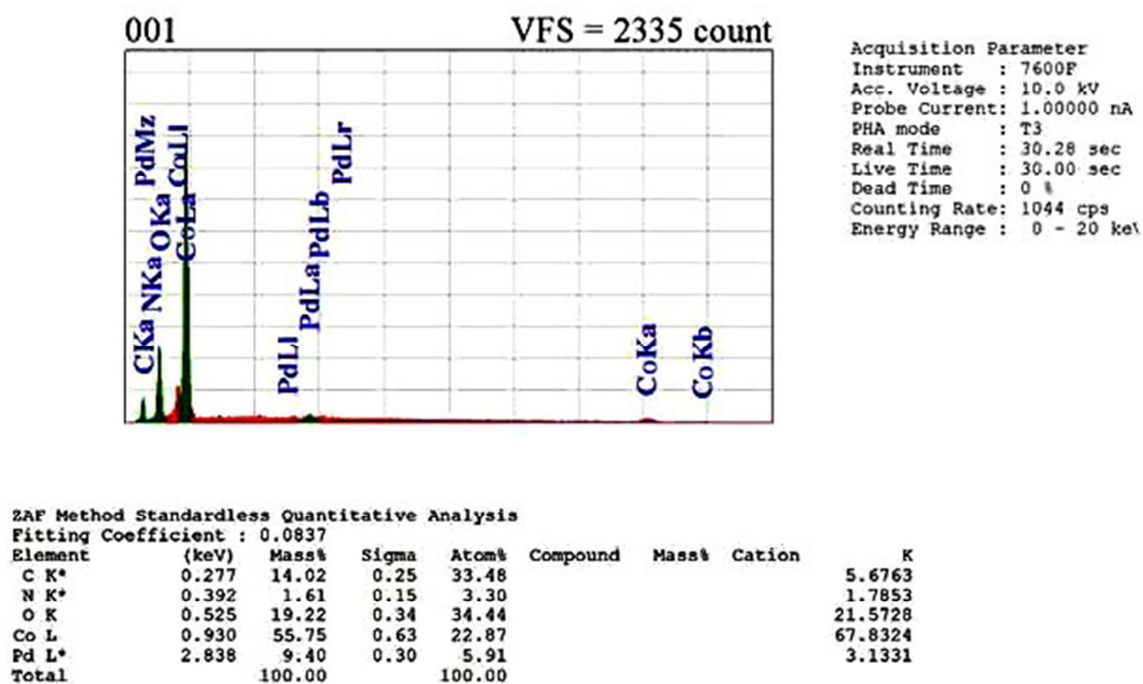


Figure 6. EDX analysis of 2,4,6-tris(di-acetamido)-1,3,5-triazine assisted bimetallic Co-Pd NPs 4.

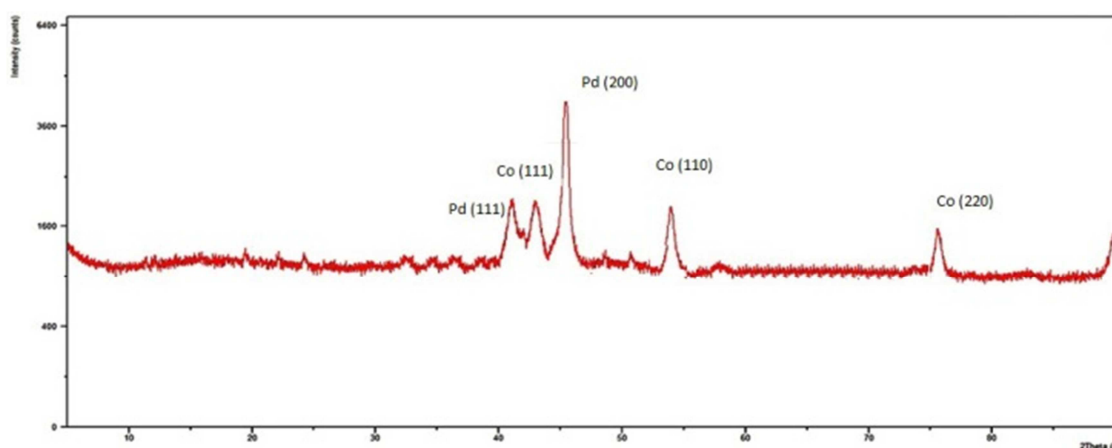


Figure 7. XRD graph of 2,4,6-tris(di-acetamido)-1,3,5-triazine assisted bimetallic Co-Pd NPs 4.

The XRD graph (Figure 7) also outlined the triazine-based Co-Pd bimetallic NPs 4 particle shape and size. Three prominent peaks of FCC Cobalt nanoparticles were related (111), (110) and (220) at 43.10° , 54.50° and 75.50° respectively associated with the Co FCC JCPDS #15-0806 standard JCPDS powder diffraction card [15] whereas the two fundamental peaks at 2θ values of 41.10° and 45.50° correlate to (111) and (200) Palladium planes respectively those represented the formation of FCC Palladium nanoparticles and, particularly in comparison to the well-known JCPDS powder diffraction card, Palladium report no (46—1043) [16]. As a consequence, these results were found in the FCC framework of triazine-based dendrimer assisted Co-Pd bimetallic NP. The dendrimer assisted Co-Pd bimetallic NPs 4 XRD pattern have been shown the average 17.50 nm particle length calculated

through the Debye-Scherrer formula whereas TEM analysis showed the average particle size of the NPs was 14.50 nm (Figure 9)

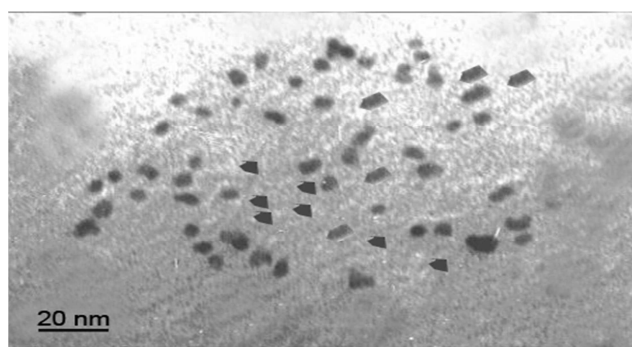


Figure 8. TEM analysis of Co-Pd bimetallic NPs 4.

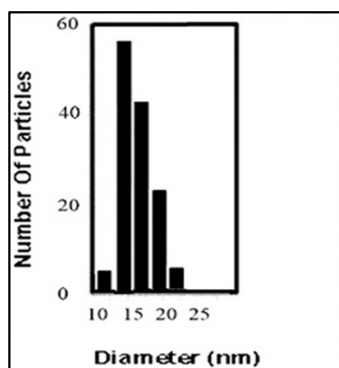


Figure 9. Particles distribution of Co-Pd bimetallic NPs 4.

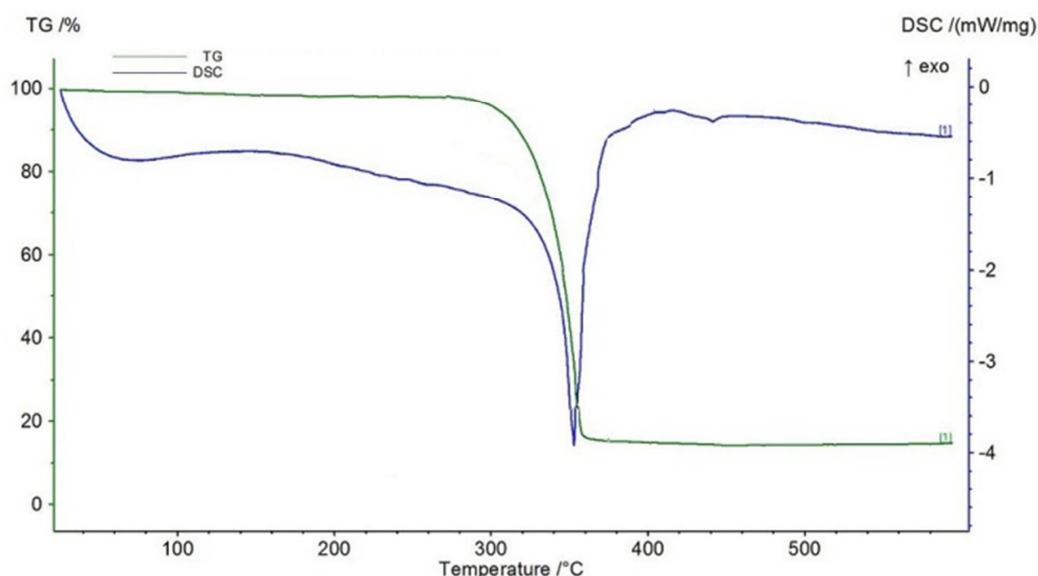


Figure 10. TG& DSC curves of 2,4,6-tris(di-acetamido)-1,3,5-triazine assisted bimetallic Co-Pd NPs 4.

3.2. Catalytic Performance of the Co-Pd Bimetallic NPs 4

In order to investigate the effectiveness of the Co-Pd bimetallic NPs 4 in Suzuki-Miyaura cross-coupling reactions, we first examined 4-iodotoluene coupling with phenylboronic acid (Figure-3) to modify reaction conditions. Different bases have resulted in different activity in the current Suzuki reaction protocol (Table 1, entries 1-6), but the most effective basis in this condition is Na_2CO_3 , which provides up to 90% isolated yield in 1h (Table 1, entry 6). In comparison with other bases, lower yields were produced (Table 1, entries 1-3). From the literature, it is well renowned that water and alcohol play a very important role in Suzuki-Miyaura reactions as a solvent [16-17]. At MeOH / H_2O (1:4) solvent mixture, Base (Na_2CO_3), Catalyst 4 (1.0 mol %) at

70°C temperature about 1.0 h, we first found 80 % yield (Table 1, entry-5). When a single type of solvents such as H_2O , EtOH, MeOH or DMF was used, the product coupling was lower than the product obtained via the EtOH / H_2O (1:4) solvent system (Table 1, Entry 6). Curiously, while in the presence of bases KOH, NaOH, K_2CO_3 , solvents EtOH, MeOH, H_2O , DMF, the temperature of up to 70°C and catalytic quantity of catalyst 4 was increased to 1.0 mol %, the yield percentage was also increased above 70 % of yield at 1.0 h (Table-1, entries 1-4). The optimized condition and excellent yield of 90 % were found in the solvent mixture EtOH / H_2O (1:4), base (Na_2CO_3), catalyst, 3 (1.0 mol %) of Figure 11 (Table 1, Entry 6) at 70°C about 1.0 h.

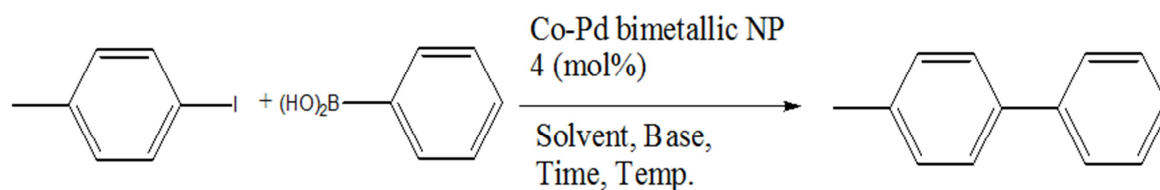


Figure 11. Optimization for the Suzuki-Miyaura reaction between 4-iodotoluene and phenyl boronic acid catalyzed by Co-Pd bimetallic NP 4.

Table 1. Optimization for the Suzuki-Miyaura reaction between 4-iodotoluene and phenyl boronic acid catalyzed by Co-Pd bimetallic NP 4.

Entry	Time	Temp.	Solvent	Base	Catalyst 4 (mol%)	Yield%
1	1.5	RT	EtOH	K ₂ CO ₃	0.5	25
2	1.0	60	MeOH	KOH	0.5	50
3	1.0	70	H ₂ O	NaOH	1.0	50
4	1.0	70	DMF	K ₂ CO ₃	1.0	75
5	1.0	70	MeOH/H ₂ O (1:4)	Na ₂ CO ₃	1.0	80
6	1.0	70	EtOH/H ₂ O (1:4)	Na ₂ CO ₃	1.0	90

Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol), Solvent (5 mL), b) Yield % of products is based on 4-iodotoluene.

However, in the presence of our catalytic system, different aryl iodides or bromides have been used as substrates under the above-optimized condition and all afford the corresponding products effectively. (Table 2, entries 1-5).

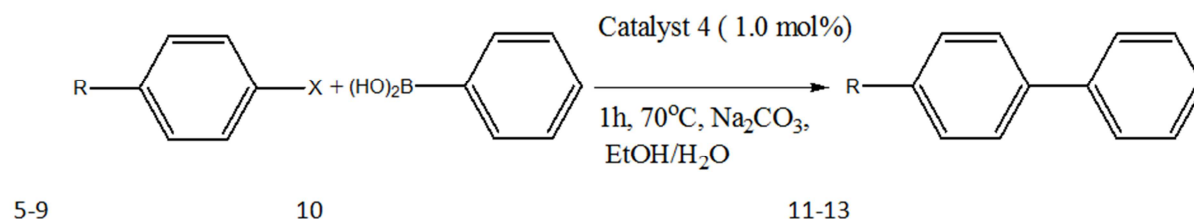


Figure 12. Different Suzuki-Miyaura reaction under optimized conditions catalyzed by Co-Pd bimetallic NPs 4.

Table 2. Different Suzuki-Miyaura reaction products under optimized conditions catalyzed by Co-Pd bimetallic NPs 4.

Entry	R	X	Yield% for cat. 4	Products
1	H	I	92	
	5	5		11
2	H	Br	90	
	6	6		11
3	CH ₃	I	90	
	7	7		12
4	CH ₃	Br	87	
	8	8		12
5	OCH ₃	I	95	
	9	9		13

Yield % of products is based on arylhalide.

All products produced through Suzuki-Miyaura coupling reactions are well known compounds and compared our acquired records with that available in the literature [14].

We also studied the recyclability of the Co-Pd bimetallic NPs 4 towards the coupling reaction between 4-iodotoluene with phenylboronic acid. During each catalytic run, black

Co-Pd bimetallic NPs **4** was recovered from the reaction mixture by filtration, washed with water and acetone, and then dried under vacuum. The recovered catalyst **4** was used for consecutive run and showed minimum decrease the yield % of products shown the following table.

Table 3. Recyclability of Co-Pd bimetallic NPs 4 for the reaction 4-iodotoluene coupling with phenylboronic acid.

Entry	Run	Time (hour)	Yield
1	Fresh	1	90
2	1	1	88
3	2	1	87
4	3	1	84
5	4	1	80

4. Conclusion

In summary, we have satisfactorily developed a convenient access catalyst for various C–C cross-coupling reactions to highly active triazine-based dendrimer supported heterogeneous Co–Pd bimetallic nanoparticles. All evaluative results (EDX, XRD, TG & DSC) confirmed the shape and size of the nanoparticle and heterogeneous catalytic activity was also found to be phosphine-ligand-free in the carbon-carbon cross-coupling reaction such as Suzuki–Miyaura coupling reactions. In addition, the introduction of high Co in the Co–Pd bimetallic nanoparticle catalyst not only decreased the catalyst's cost but also created it highly reusable for up to 5 catalytic cycles without any substantial loss in catalytic activity. The high recyclability catalyst Co–Pd bimetallic nanoparticles can also be used through the formation of C–C bonds to synthesize multiple biologically active compounds. Our ongoing effort through this work will attract the scientific community's attention to developing a class of highly active bimetallic nanoparticles catalysts, so that the use of Pd for coupling reactions can be significantly reduced by introducing a second inexpensive metal (non-noble metals), while at the same time achieving stability and preserving the catalyst's heterogeneous nature.

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Conflicts of Interest

The authors declare that they have no competing interests.

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