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ARTICLE TYPE

Self Assembled Material of Palladium Nano-particles and Thiocalix[4]arene Cd(II) Complex as Efficient Catalyst for Nitro-phenol Reduction

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A new material based on self assembly of palladium nano-particles by thiocalix[4]arene (TCA) based Cd(II) complex is synthesized. Hydrophobic interactions between *tert*-butyl groups on either ends of TCA- cadmium complex and palladium nano particles generate self assembled material **5**. The material shows its potential application as heterogeneous recyclable catalyst for reduction of 4-nitro phenol (4-NP). The rate constants for the catalyst **5** observed in 1st and 5th catalytic cycle was 0.117 min⁻¹ and 0.109 min⁻¹ respectively reveals the efficiency of the catalyst.

1 Introduction

Noble metal nano-particles such as palladium (Pd) with controlled size, shape, and surface structure are of fundamental importance because of their unique properties and numerous promising applications.¹⁻⁶ The preparation of shape controlled noble metallic (Pd, Pt, Rh) nano-particles has led to catalytic systems with high potentialities.⁷⁻¹¹ The shape controlled formation of metallic nano-systems can be achieved through adsorption of surfactants, ligands or polymers.^{12,13} One of the efficient methodologies for generation of organized nano-architectures involves the utilization of macrocycles.¹⁴⁻¹⁸ Among various macrocycles used for developing such assemblies, calix[4]arenes have been one of the most promising candidates.¹⁹⁻

²² Thiocalix[4]arene exhibits different chemical and physical properties as compared to calixarenes.²³⁻²⁵ One of the capabilities of thiocalixarene is its strong interaction towards a wide range of metal ions because of the presence of bridging sulfur atoms. Thiocalixarene based metal complexes have been well known for their catalytic efficiency in organic reactions like [2+2+2] cycloaddition of terminal alkynes, polymerization of ethylene and oxidation of alcohols e.t.c.²⁵ However, in the current manuscript we have utilized thiocalixarene based metal complex as a template for generation of new self assembled material which works as catalyst for reduction of 4-NP (*vide infra*).

Our research work focuses on development of new organic-inorganic hybrid systems for various applications.²⁶⁻³⁰ In the present manuscript, we aimed at controlled synthesis of new palladium nano-particle architecture using thiocalixarene as template. Therefore, we preferred to use Cd (II) polynuclear complex³¹ of thiocalix[4]arene (**3**) as template. The rationale was to use the hydrophobic *tert*-butyl moieties at either ends of **3** to interact with metal nano-particles/aggregates. Further, the synthesized material {**3** stabilized palladium nano-particles (named as **5**)} was further used as catalyst for 4-nitro phenol (4-

NP) reduction.

4-NP is highly significant compound/pollutant in various industrial processes. 4-NP is highly toxic and because of its high solubility in water, it is present in industrial discharges from industries synthesizing pesticides, insecticides and synthetic dyes.^{32,33} Because of its highly carcinogenic nature, it has been listed as one of the main industrial pollutant by US environmental protection agency.³⁴ In addition, its reduced product 4-amino phenol has important applications in synthesis of analgesic and antipyretic drugs.³⁵ Therefore, degradation of 4-NP and synthesis of 4-amino phenol simultaneously are of utmost importance. Different processes have been utilized for removal of 4-NP such as adsorption, microbial degradation, photocatalytic degradation, microwave assisted catalytic oxidation, electrochemical treatment³⁶⁻⁴¹ and reduction of 4-NP.⁴²

Recently, palladium metal nano-particles have attracted lot of attention as catalyst due to their high activity and efficiency.^{43-45,4,35} These features of palladium metal nano-particles and the significance of 4-NP reduction prompted us to utilize synthesized material **5** for reduction of 4-NP. The material **5** shows a good recyclability as a catalyst for 4-NP reduction (*vide infra*). To the best of our knowledge, the utilization of thiocalixarene templated self assembly of palladium metal nano particles as catalyst for reduction of 4-NP is unprecedented.

2 Experimental

2.1 Materials and instrumentation

All chemicals and reagents were purchased from Sigma Aldrich. The IR spectral studies were performed on Perkin Elmer FT-IR spectrometer using KBr pellets. UV-vis studies were carried out on SHIMADZU UV-2450 spectrophotometer using quartz cuvettes. Powder X-ray diffraction (PXRD) data were collected on Rigaku Smart Lab 9 KW rotating anode Powder X-ray Diffractometer at room temperature. Single crystal X-ray

diffraction data were collected on a Bruker AXS D8 Venture diffractometer with X-ray generator operating at 50 kV power and 1 mA current using graphite monochromated MoK α ($\lambda = 0.7107 \text{ \AA}$) radiation containing CMOS detector (for details see supporting information page S2). The thermo gravimetric analysis was carried out using NETZSCH STA 449F1 JUPITER SERIES under N₂ atmosphere and at a heating rate of 10 °K/ min. TEM images were collected on SEI TECNAI F20 HRTEM instrument.

2.2 Synthesis of Pd self assembly (5)

A mixture of **3** (20 mg, 0.10 mM) and palladium(II) chloride (18 mg, 1.02 mM) in 100 ml ethanol was sonicated at 35 °C for 15 min. The solution became dispersed on sonication and this dispersion was kept for 48 h. During this time, the solution turned from yellow to black in color which was used for TEM and DLS analysis.

2.3 Preparation of samples of 5 for FTIR, TGA and PXRD analysis

We centrifuged the above colloidal black color solution. The black color material settled down with an upper transparent layer of ethanol. We decanted off the ethanol and the black colored material (**5**) thus obtained was dried at 40 °C for 4h and was used for FTIR, TGA and PXRD analysis.

2.4 Catalytic reduction of p-nitro phenol with catalyst 5

To a stirred 10 ml aqueous solution of 4-NP (1 mM) in a round bottom flask, 10 mg of NaBH₄ was slowly added. The UV-Vis absorption of 3 ml of the above solutions of 4-NP (1 mM) in absence and presence of NaBH₄ was taken in a quartz cuvette. Subsequently, 0.5 mg of heterogeneous catalyst **5** was added to the above round bottom flask. The 3 ml of the resulting solution was transferred into a quartz cuvette and the UV-Vis absorption studies were performed with a time interval of 1 min. After 16 min, we recycled the catalyst **5** from round bottom flask by centrifugation and dried at 40 °C for 4h. This complete cycle was repeatedly done for five times and after completion of fifth cycle the stability of catalyst **5** was confirmed by FTIR and PXRD.

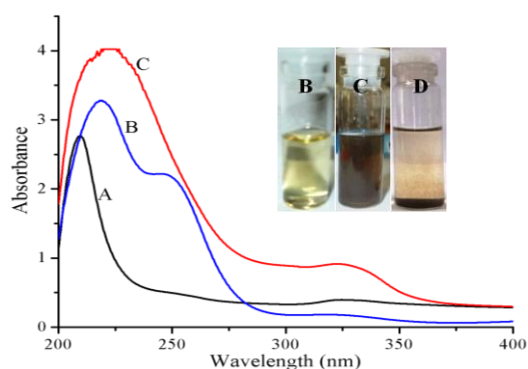
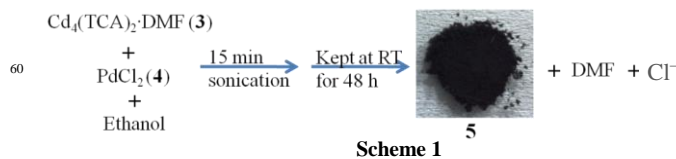


Figure 1. UV-visible spectra of (A) Solution of **3** (0.10 mM) in ethanol. (B) **4** (1.02 mM) in ethanol. (C) **5**. Inset shows the color of the solutions with respect to solution **B** and **C**. **D** represents the color of mixture of **4** & **2**.



Scheme 1. Synthesis of **5**

2.5 Procedure for reduction of 4-nitrophenol on silica by 5

The solution of 100 μL of 4-NP solution was adsorbed on silica. Afterwards, 20 μL of **5** (0.5 mg in 1 ml) was added to it to observe the change in color.

3 Results and discussion

3.1 Synthesis and characterisation

75 Thiocalixrene Cd (II) complex **3** {Cd₄ (TCA)₂}.DMF (see supporting information page S3 and S4) was synthesized by solvothermal reaction of CdCl₂ and thiocalix[4]arene³¹ in dimethylformamide (DMF) as solvent (scheme 1). Ethanolic dispersion (100 ml) of **3** (20 mg, 0.10 mM) and solution of PdCl₂ (18 mg, 1.02 mM) was sonicated at 35 °C for 15 min. As polar solvents have been reported as mild reducing agents⁴⁶⁻⁴⁹ for synthesis of palladium nano-aggregates, we decided not to use any additional reducing agents and left the solution for prolonged hours in ethanol at room temperature. We observed that after 48 h, the solution turned from yellow to black coloured⁴⁶ colloidal solution indicating the formation of palladium nano- particles or aggregates (figure 1). The colloidal nature of the solution indicates that the palladium particles or aggregates have been stabilized by **3**. The UV-vis spectrum of ethanolic solution of **3** and PdCl₂ (**4**) showed absorption band at 209 nm, 216 nm and 245 nm (figure 1A and 1B) respectively. The mixture of both the solutions of **3** and PdCl₂ (**4**) generating **5** (figure 1C) showed absorption bands at 221 nm with red shifted absorption band at 324 nm.

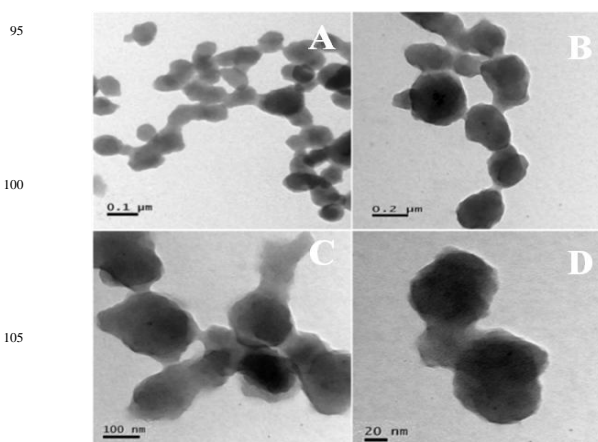


Figure 2. TEM images of **5** under different magnifications.

To have an insight in to the mode of interaction between **3** and **4**, we carried out the TEM studies. The TEM images of the black colored colloidal solution of **3** and **4** (figure 2) showed an organized network of palladium aggregates (figure 2A-D). The aggregates of palladium nano-particles stabilized by **3** were held

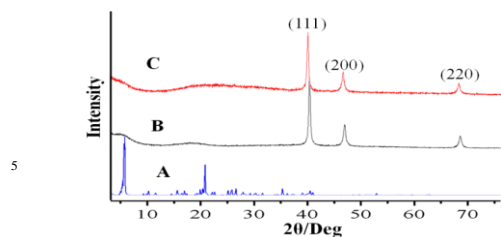


Figure 3. PXRD of (A) **3** (B) **5** (C) **5** after 5th run.

together in an organized fashion generating a self assembly. The DLS analysis of the black colored solution of **5** (*vide supra*) showed the particle size in range from 90-410 nm ($PDI = 0.1$) indicating the formation of aggregates or assembly of palladium nano-particles (see supporting information page S7). The presence of **3** in **5** was also indicated by EDX analyses. The EDX spectrum of self assembled aggregates shows the presence of cadmium, sulphur, palladium and carbon (see supporting information page S8).

We also performed reaction of $PdCl_2$ (**4**) with lesser concentration of **3** (10 mg, 0.05 mM) under similar conditions. This resulted in the precipitation of black particles that settled down leaving a clear solvent (image shown in supporting information page S9) unlike the earlier experiment in which higher concentration of **3** resulted in a colloidal solution.

To confirm that material **5** is an integrated assembly of **3** & **4**, we performed TGA analysis of **3** and **5**. The TGA analysis of **3** shows (see supporting information page S5) a degradation curve from 135 °C to 205 °C with 11.61% weight loss corresponding to the loss of DMF molecules. Next degradation curve is observed from 465 °C to 770 °C corresponding to degradation of organic moieties with 61.74% weight loss. The residual mass 23.84 % corresponding to metal oxides or sulfide are left behind. Contrary to this, the TGA curve of **5** showed (see supporting information page S5) no degradation corresponding to DMF molecule indicating the removal of DMF while generation of self assembly with Pd nano-particles. Degradation curve is observed from 240 °C to 455 °C corresponding to degradation of organic moieties with 61.85 % weight loss with remaining residual mass (47.58 %). The comparable percentages of organic moieties in both the samples confirms the presence of thiacalix(4)arene in **5**. The increase in the residual mass content in **5** is attributed to the presence of Pd metal in **5**. Further, we carried out PXRD studies for **3** and **5** (figure 3A and 3B). The XRD pattern of the obtained product **5** showed the characteristic diffraction peaks of palladium face-centered cubic (fcc) phase, indicating the formation of metallic palladium.⁴⁶ We also performed the IR analysis of **3** and **5**. The IR spectrum of **3** showed stretching band at 1679 cm^{-1} corresponding to DMF molecule (see supporting information S6). The absence of this band in the IR spectrum of **5** (see supporting information S6) indicates the removal of DMF molecules while formation of palladium metal self assembly. In addition, the presence of bands corresponding to **3** in the IR spectrum of **5** confirms the presence of **3** in **5**.

3.2 Possible mechanism of formation of palladium self assembly

We believe that effective hydrophobic interactions^{50,51} between

the non polar *tert*-butyl groups on either ends of **3** and embryonic nano-particles lead to their stabilization and limit the growth of the aggregates in a controlled manner. The growth of aggregates is also influenced by the variation of the surface energy with size and the particles tend to grow into a spherical shape in order to minimize their surface energy⁵². The stabilization of the aggregates on either ends of the **3** leads to a chain like phenomenon resulting into an organized network as visualized in TEM images. To explore the role of sulphur atoms in generating the self assembled material **5**, we carried the similar experiments with native thiacalix(4)arene molecule (**2**) and $PdCl_2$ (**4**). We observed that **2** was unable to stabilize palladium particles which ultimately settled down (figure 1D). The primary difference between **2** and **3** is the presence of terminal hydrophobic alkyl ends present at the either ends only in **3** which leads to the self assembly behaviour with palladium nano-particles.

3.3 Catalytic activity of **5** for reduction of 4-nitrophenol

We evaluated the catalytic efficiency of **5** for reduction of 4-nitrophenol (4-NP)⁵³ to 4-aminophenol (4-AP) in presence of $NaBH_4$ and water as a solvent. The characteristic absorption band of 4-NP (1 mM) was observed at 317 nm (figure 4). On addition of $NaBH_4$ (10 mg) new red shifted band (figure 4) at 400 nm corresponding to phenolate ion is observed. On addition of small amount of catalyst **5** (0.5 mg), the decrease in the absorption was observed (figure 4) on time scale. Every minute the significant decrease in absorption intensity was observed with formation of new blue shifted band at 300 nm corresponding to 4-AP (figure 4) with isosbestic points⁵⁴ at 314 and 281 nm and the reduction process was completed in 16 min (figure 4). We observed that in absence of catalyst **5**, $NaBH_4$ could not convert phenolate ion in to 4-AP even after 19 min on time scale (see supporting information page S11) proving the efficiency of the **5** as catalyst for 4-NP reduction. The reduction process was also observed with naked eye colour changes (figure 5A). In order to confirm the heterogeneous nature of the catalyst we carried out the standard leaching experiment (see supporting information page S12).

The reduction kinetics were monitored by UV-vis absorption spectroscopy of the reaction mixture after the addition of the catalyst **5**. As the reaction proceeds, the absorbance of phenolate ion at 400 nm started decreasing along with a related increase in the 300 nm peak corresponding to 4-AP (conversion time 16 min, figure 5B). The high concentration of $NaBH_4$ used in the reaction in comparison to the concentration of 4-NP indicates the lowering of decomposition rate of $NaBH_4$ ensuring the first order rate kinetics^{42,55,56} which can be demonstrated by equation 1.

$$-dc_t/dt = k_a c_t \quad (\text{equation 1})$$

where c_t was 4-NP concentration at any time, after **5** was added;

k_a was the rate constant. 4-NP concentration was proportional to the intensity of its absorption band. Thus, equation 1 can be expressed as

$$-d \ln A_t = k_a dt \quad (\text{equation 2})$$

$$\therefore -d \ln A_t/A_0 = k_a t \quad (\text{equation 3})$$

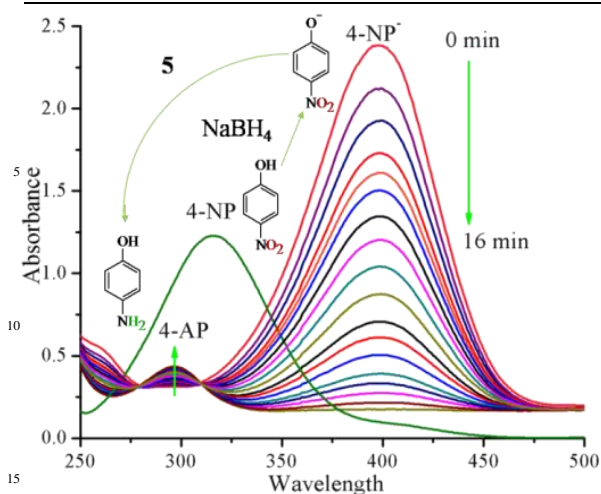


Figure 4. Time dependent evolution of UV-vis spectra showing the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by **5**.

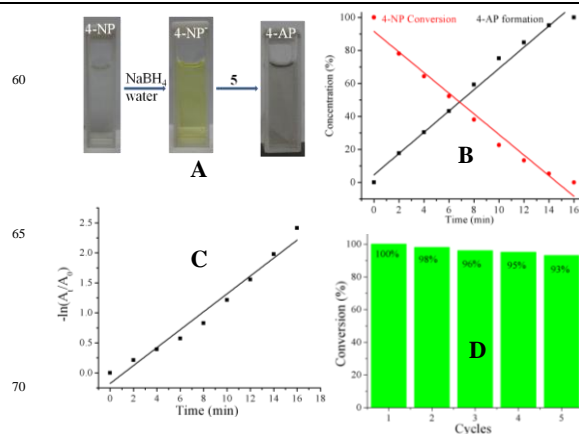


Figure 5. (A) Naked eye changes observed during conversion of 4-NP to 4-AP. (B) Kinetics of the reduction reaction of 4-NP to 4-AP. (C) Plot of $-\ln(A_t/A_0)$ vs t for conversion of 4-NP to 4-AP with **5**. (D) Conversion of 4-NP to 4-AP during 5 cycles by **5** with 16 min time duration.

most of the reported catalysts, a gradual significant decrease of rate constant k_a was observed with repeated cycles whereas in present work rate constant k_a observed in 1st and 5th catalytic cycle was 0.117 and 0.109 min^{-1} respectively. Therefore, the decrease in the rate constant k_a for the nitro phenol reduction is very less in comparison to the already reported catalysts and proves its high catalytic efficiency of **5**.

3.4 Reduction of 4-nitrophenol on silica by **5**

We explored the possibility of utilizing catalyst **5** for reduction of 4-NP in environment and thus, we planned to test the **5** in presence of silica. We dispersed the silica on glass slide and adsorbed the solution of 1 mM of 4-NP and NaBH_4 on it. Initially the silica was of bright yellow color (figure 6A). But the moment we added few drops of dispersion of **5** (figure 6B) in H_2O , it started changing its color from yellow (4-NP) to colorless (4-AP). It suggests that the catalyst **5** is an efficient catalyst for reduction of 4-NP in the presence of solid and environmental samples.

4 Conclusions

To conclude, we have synthesized a new thiacalix[4]arene based self assembled material which behaves as an efficient catalyst for reduction of 4-nitrophenol to 4-aminophenol. The utilization of TCA complex as a template for self assembled materials through hydrophobic interactions may prompt other researchers working on calixarene/thiacalixarene materials to utilize metal complexes of the scaffold in generation of new self assembled materials for wide variety of applications.

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Notes and references

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where A_t and A_0 are the intensities of 4-NP absorption bands at $t = t$ and $t = 0$ (namely catalyst, no catalyst), respectively.

Figure 5C represents correlation between $-\ln(A_t/A_0)$ vs time (min) for conversion of 4-NP to 4-AP with **5**. The linear correlation indicates that the above reaction is ruled by first order kinetics and thus $k_a = 0.117 \text{ min}^{-1}$ which is easily determined from the slope of the line. We also compared the rate constant of **5** with Pd composite obtained from reaction of PdCl_2 (**4**) with lesser concentration of **3** (10 mg, 0.05 mM) ($k_a = 0.096 \text{ min}^{-1}$) (see supporting information S9) and Pd(0) obtained from reaction of **4** and NaBH_4 in water ($k_a = 0.059 \text{ min}^{-1}$) (see supporting information S10). These rate constants were 1.22 and 1.98 times lesser than from rate constant (k_a) of **5**.

The catalyst **5** was also checked for its recyclability. The catalyst **5** showed excellent recyclability giving yields over 92% even after 5 cycles ($k_a = 0.109 \text{ min}^{-1}$) estimated time 16 min (figure 5D). The stability of the reused catalyst **5** was further confirmed by PXRD and IR studies. The PXRD and IR of **5** were similar even after 5th cycle (figures 3C and see supporting information S6).

We propose that during the conversion of 4-NP to 4-AP in presence of **5**, initially the NaBH_4 converts 4-NP to phenolate ion. The hydride ions adsorbed on the surface of palladium metal aggregates are transferred to the nitro group of the aromatic ring.^{42,57,60} The nitro group is reduced to nitroso species. Further, the same process of reduction is repeated twice reducing nitroso species in to hydroxylamine and eventually forming primary amine 4-AP.^{42,61,62}

We also compared catalytic activity of **5** with previously reported Pd(0) composites (see page S13 of supporting information). In

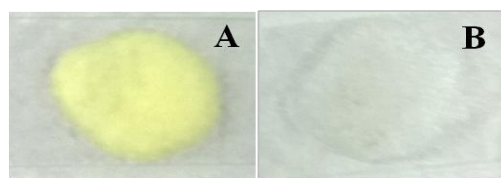
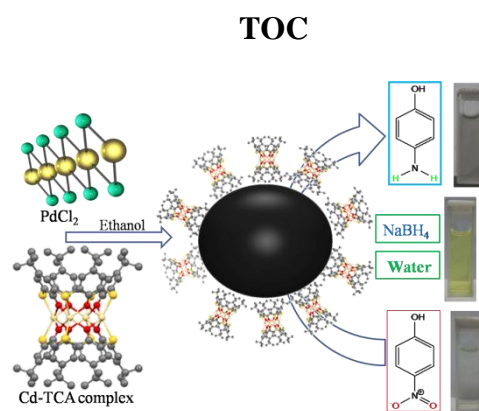


Figure 6. 4-nitrophenol (4-NP) reduction on silica by **5**, (A) Adsorption of 4-NP solution with NaBH_4 , (B) After addition of **5**.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Cadmium complex based on thiacalix[4]arene scaffold is utilized to synthesize material with palladium nano-particles which behaves as an efficient catalyst for conversion of 4-nitrophenol to 4-aminophenol.