Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

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

Darsi Rambabu, Chullikkattil P. Pradeep, Pooja, Abhimanew Dhir*

Indian Institute of Technology, Mandi, Himachal Pradesh, India.

Experimental

X-ray crystallographic data collection and refinement of the structure: Single crystal X-ray diffraction data of compound **3** 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 MoKα (λ = 0.7107 Å) radiation containing CMOS detector. Data reduction and integration were performed by SAINT V7.685A12 (Bruker AXS, 2009) and absorption corrections and scaling was done using SADABS V2008/112 (Bruker AXS). The structure was solved by direct methods and refined by a full-matrix least squares techniques using SHELX 97[RS1]with anisotropic thermal parameters for selected atoms. Hydrogen atoms were introduced in calculated positions and included in the refinement riding on their respective parent atoms.

RS1. G. M. Sheldrick, *ActaCryst*., 2008, **A64**, 112.

Experimental Procedure

Synthesis of $[Cd_4(TCA)_2]$·DMF (3): We synthesized 3 according to slightly modified procedure.[RS2] A mixture of 0.170 g (0.92 mmol) $CdCl_2$ **(1)**, 0.167 g (0.23 mmol) of thiacalix[4]arene (H_4TCA) **(2)** and 6 ml of DMF were placed in Parr's acid digestion bomb and it was kept in oven at 125°C for 48 h. The mixture was allowed to cool gradually at room temperature for 12 h to obtain transparent colorless needle like crystals (0.094 g, yield 43.3%, according to TCA), washed with cold DMF (3×1 ml) and dried under vacuum at room temperature.

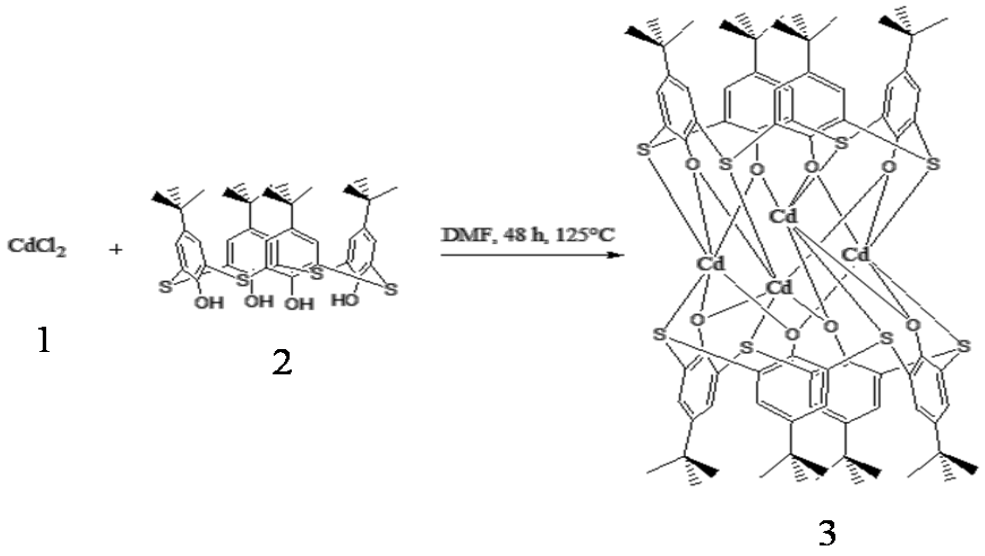

Figure **S1**: Schematic representation of synthesis of **3**.

RS2. M. L. Fu, N. L. Rangel, R. D. Adams, J. M. Seminario, *J. Clus. Sci.*, 2010, **21**, 867.

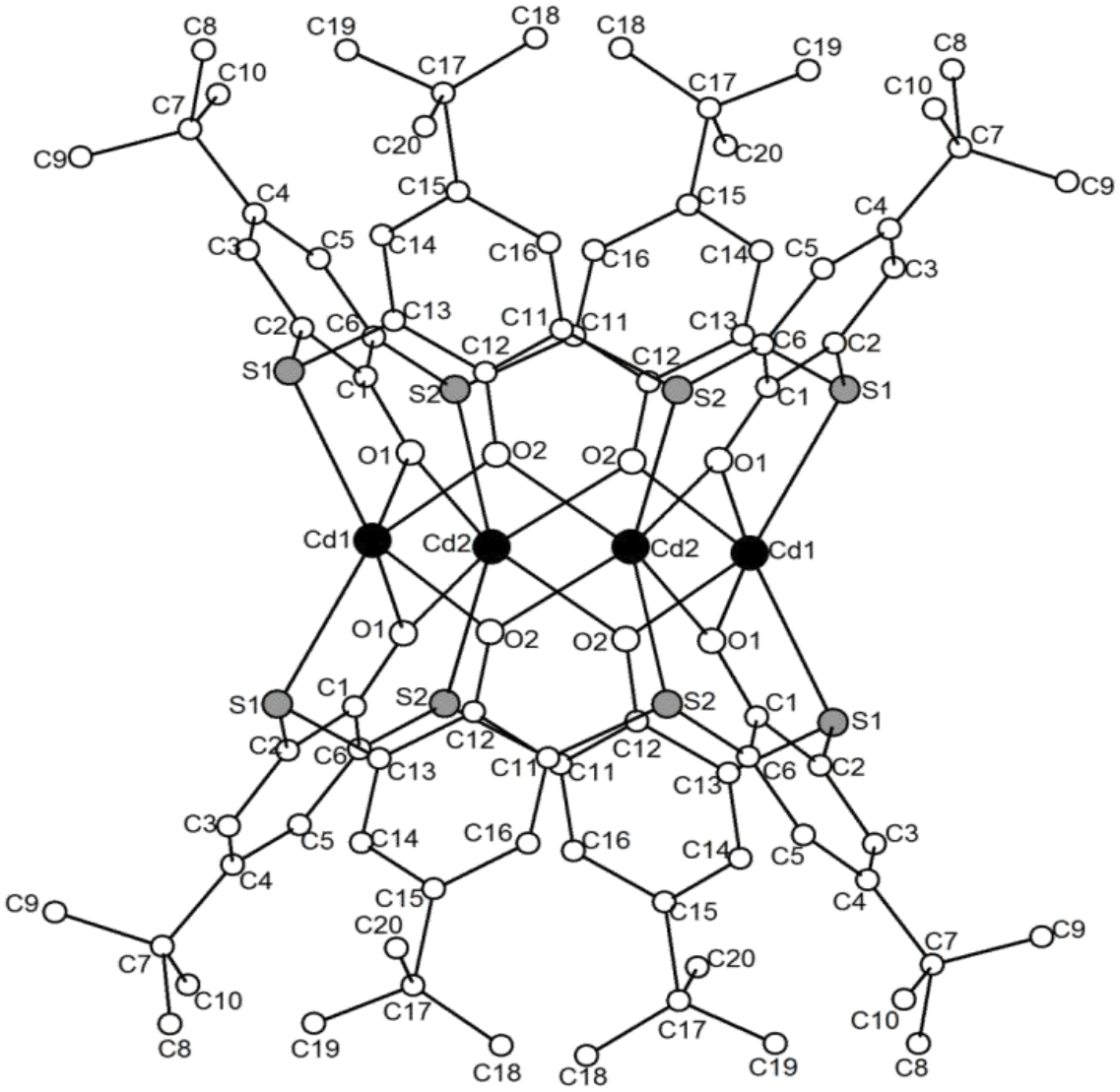

Figure **S2**: Crystal structure for **3.**

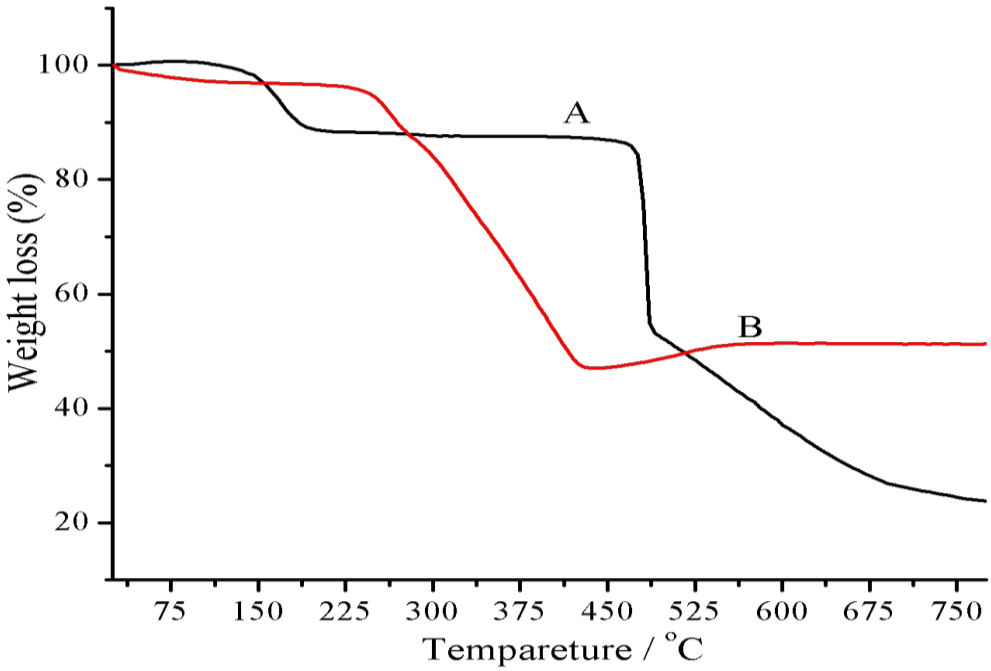

Figure S3. TGA curve for (**A**) **3** (B) **5.**

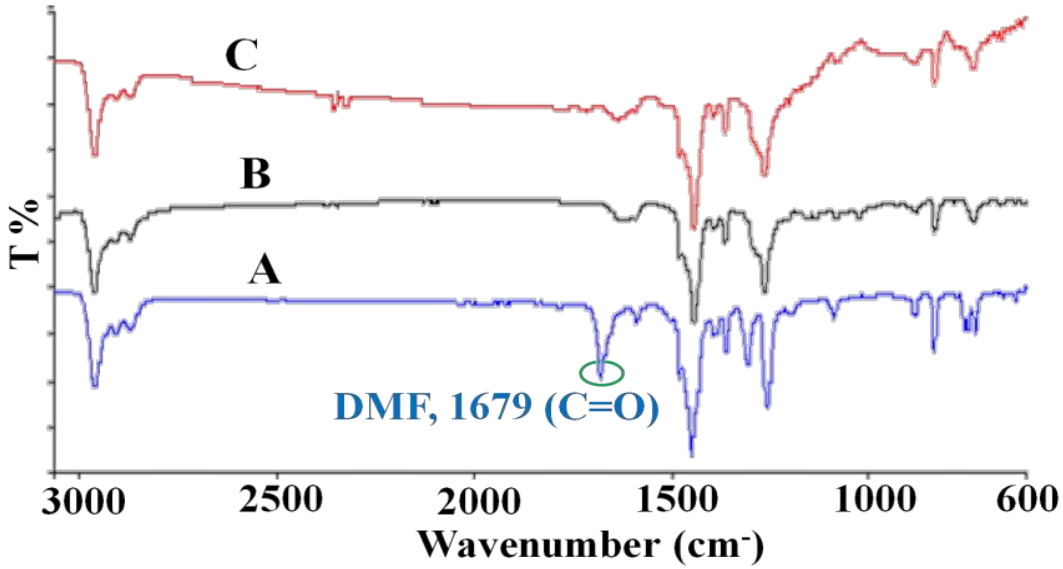

Figure S4. IR spectrum of (**A**) **3** (B) **5** (C) **5** after 5th run.

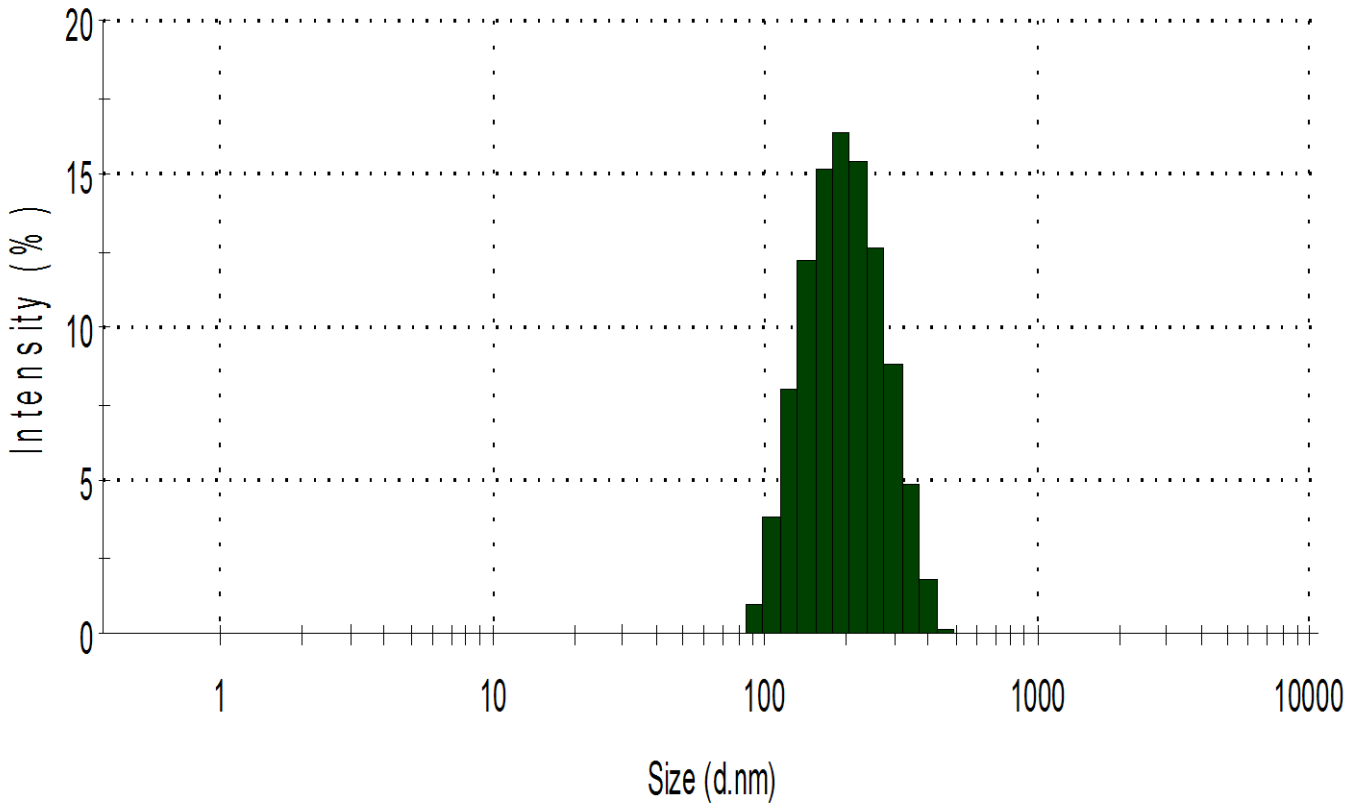

Figure S5. DLS data (size distribution) of **5**.

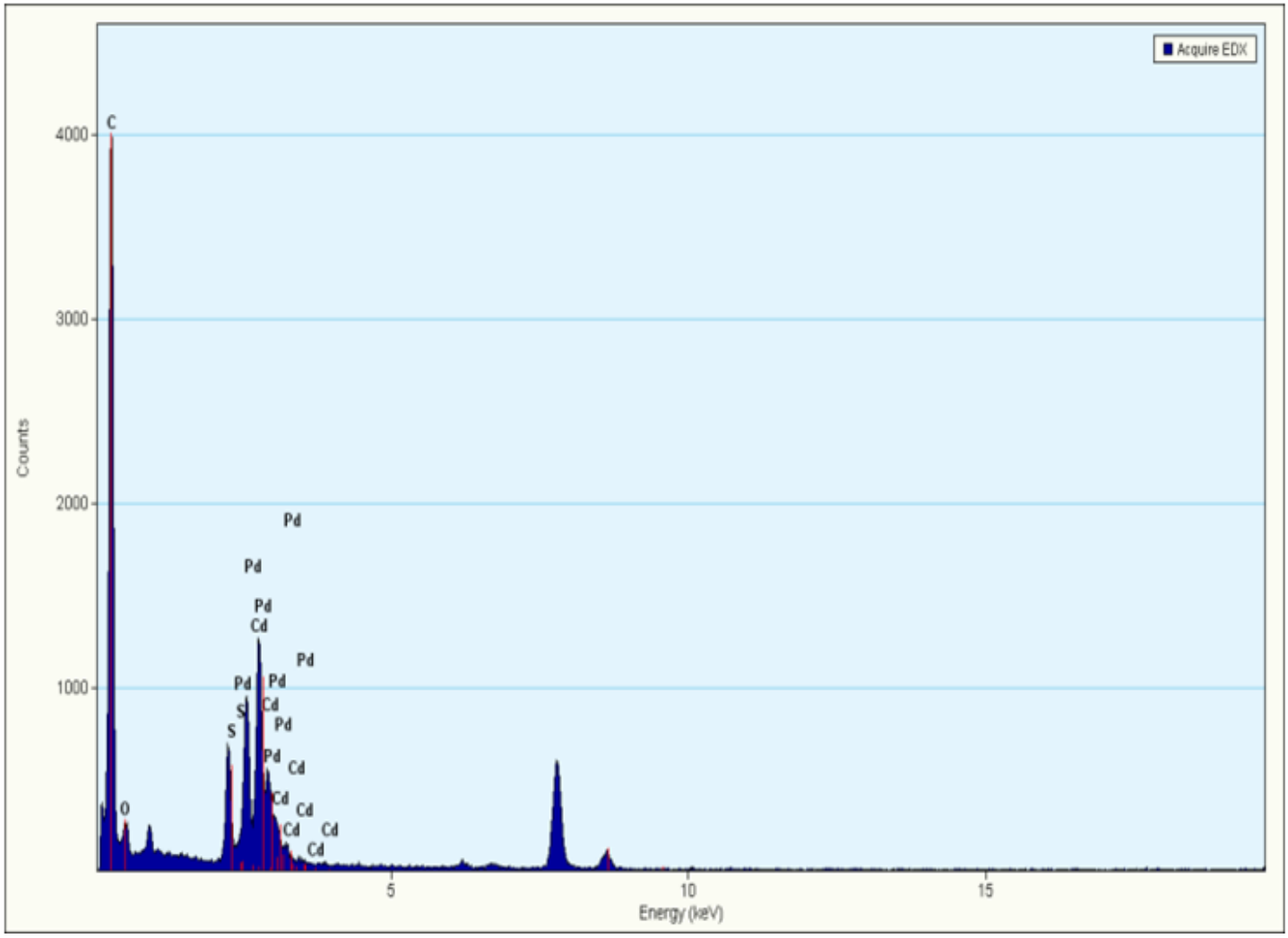

Figure S6. The EDX spectrum for catalyst **5**.

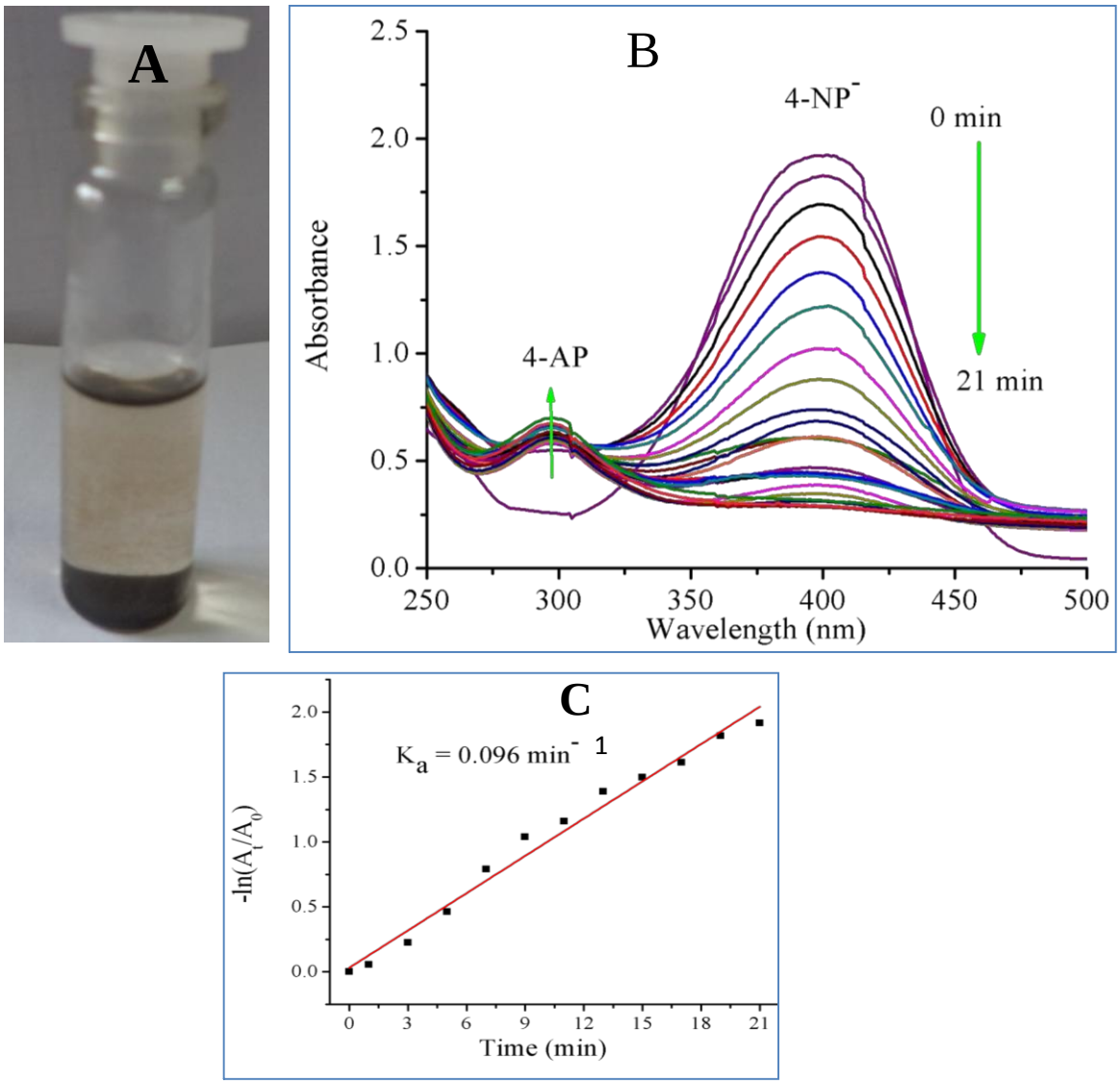

Figure S7. (A) Photograph, (B) Time dependent evolution of UV-vis spectra showing the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and (C) Plot of $-ln(A_t/A_0)$ *vs* t for conversion of 4-NP to 4-AP by Pd composite obtained from (1.02 mM) $PdCl_2$ (**4**) with lesser concentration of **3** (10 mg, 0.05 mM) in 100 ml ethanol solution.

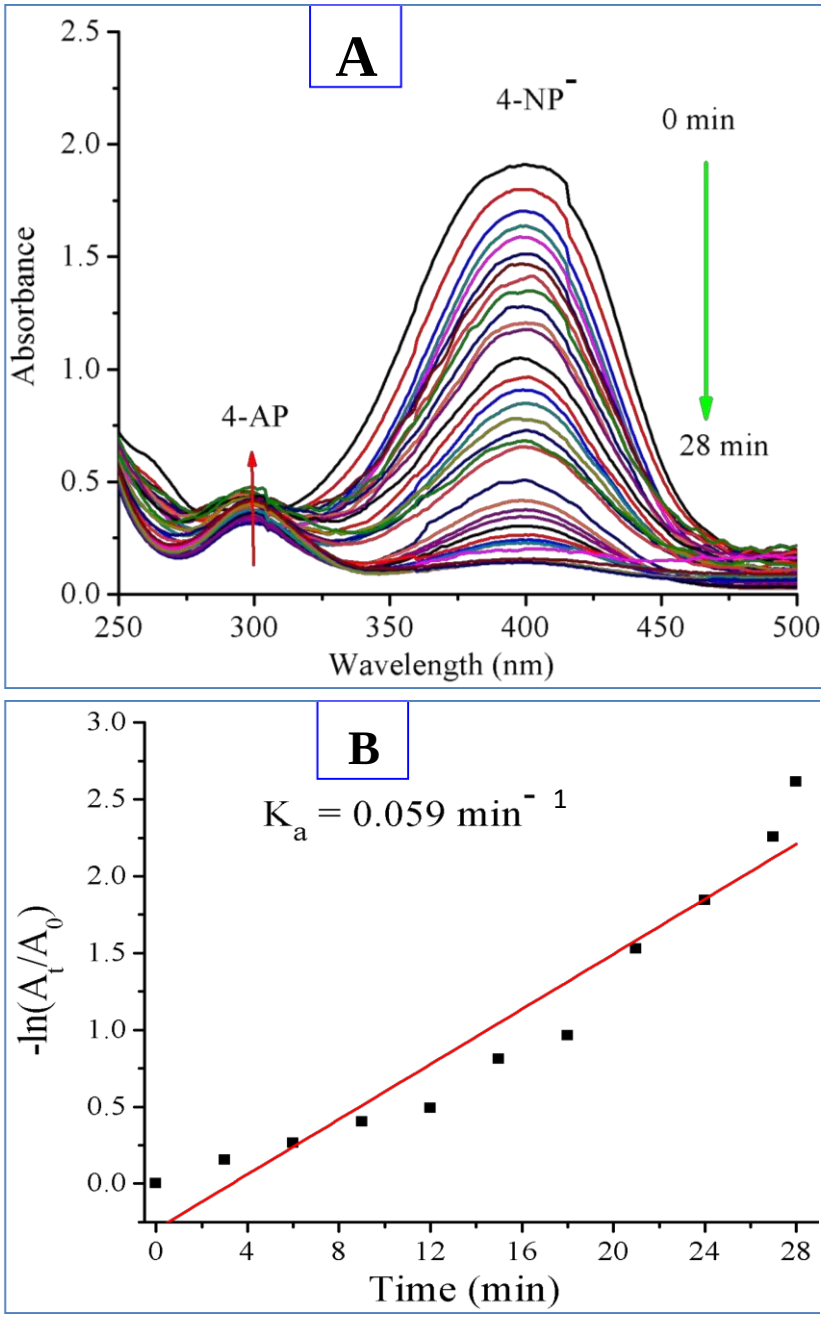

Figure S8. (A) Time dependent evolution of UV-vis spectra showing the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and (B) Plot of $-ln\ (A_t/A_0)$ *vs* t for conversion of 4-NP to 4-AP by Pd(0) obtained from reaction of $PdCl_2$ and $NaBH_4$ in water.

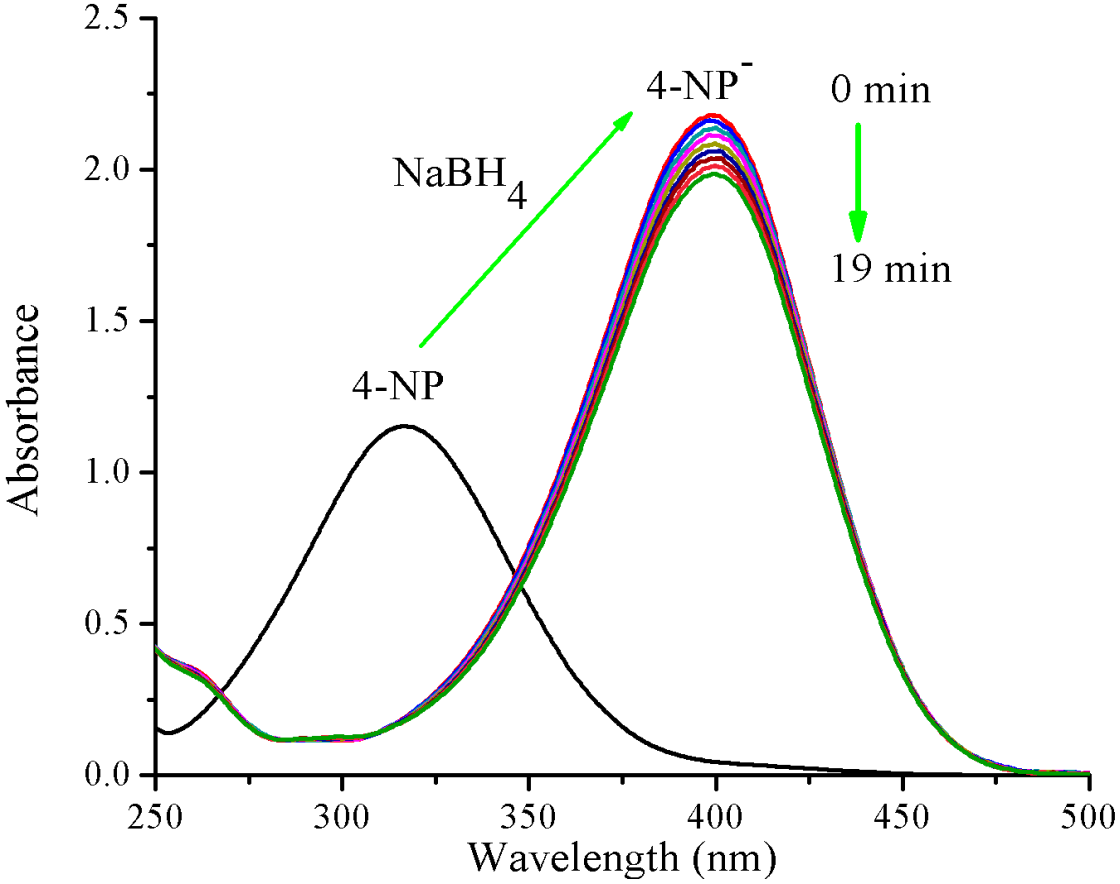

Figure S9. The time dependent UV-vis spectra of 4-nitrophenol in the presence of $NaBH_4$.

Catalyst leaching experiment for catalyst 5: For the stability and heterogeneity of Pd nano aggregates in **5**, we performed leaching experiment. In this test, 10 mg of catalyst **5** and 5 ml water was added in beaker and stirred for 1 h at room temperature, after stirring it was filtered. The colorless filtrate indicated there was no Pd aggregates. Further we added 4-NP and $NaBH_4$ to filtrate and observed that there is no reduction taken place even after 20 min through Uv-vis sprectascopy. Absence of any minute 4-AP was confirmed heterogeneity and no leakage of catalyst **5.**

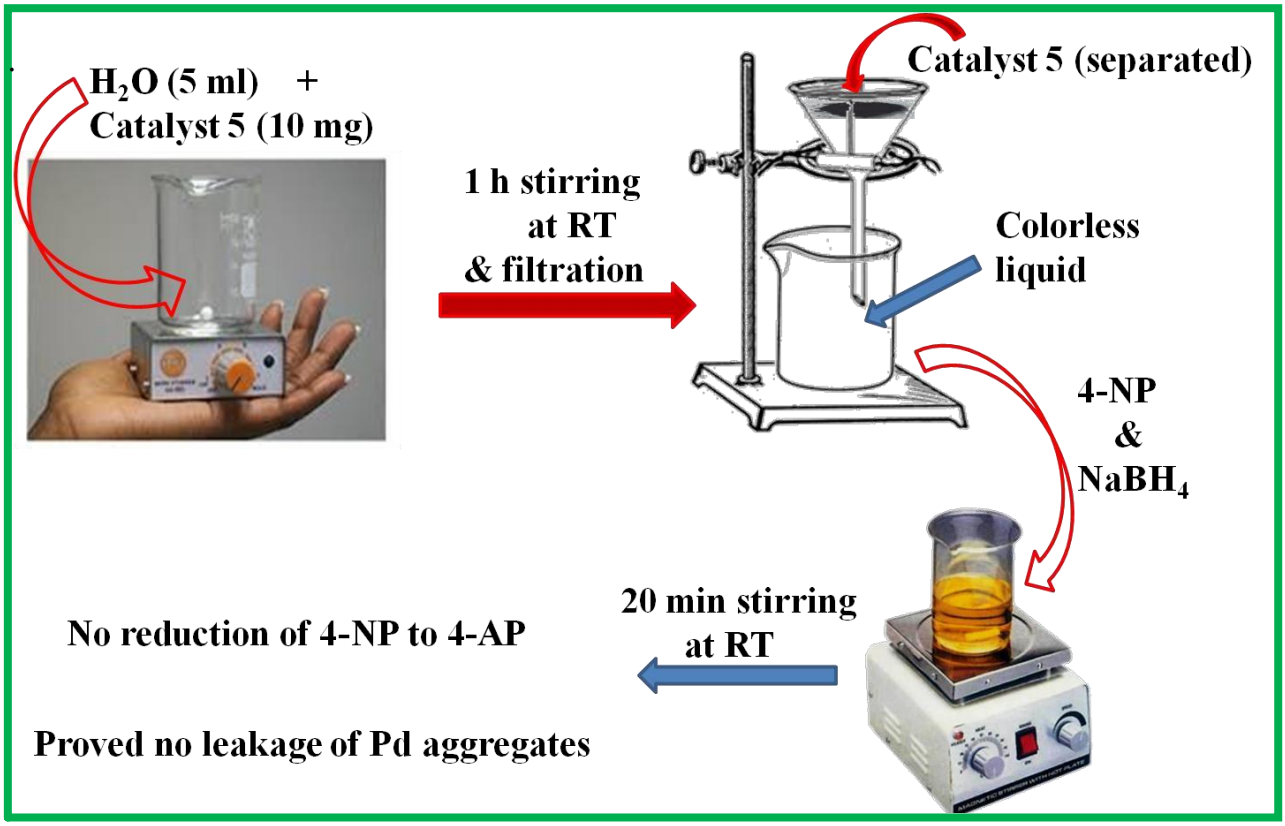

Figure S10. The leaching experiment for **5**. Catalyst **5** was stirred at RT for 1 h in water and filtered. The reduction of 4-NP with filtrate was performed by UV-vis. In addition, absence of 4-AP confirmed no leakage of catalyst **5.**

Table S1: Comparison of Pd nanoparticles from previously reported, for the 4-NP reduction:

S.No.	Pd(0) composite	Conc of 4-NP (mM)	Conc of Pd(0)	Rate const k_a (min^{-1})	Runs, & k_a (min^{-1}) after last run	Technique used for determination stability of catalyst	Reference
1	Pd(0)@CdTCA (**5**)	1.0	50 µg	0.117	5 cycles, k_a = 0.109	Stable after 5th run confirmed by FTIR and PXRD	This work
2	$Pt_{55}Pd_{38}Bi_7$ NWs	0.087	15µg	0.009	----------	----------	RS3
3	$Pt_{41}Pd_{52}Bi_7$ NWs	0.087	15µg	0.076	----------	----------	RS3
4	$Pt_{26}Pd_{67}Bi_7$ NWs	0.087	15µg	0. 232	----------	----------	RS3
5	$Pd_{92}Bi_8$ NWs	0.087	15µg	0.143	----------	----------	RS3
6	$Pt_{1.4}Pd_1$	0.087	15µg	0.258	----------	----------	RS3
7	Polypyrrole/TiO2/Pd	0.107	29 µg	0.738	8 cycles, k_a = 0.428	----------	RS4
8	PdNCs/SnO2-GNS	0.161	0.00452 mM	1.218	10 cycles, $k_a \approx$ 0.8	----------	RS5
9	Pd/SBA15	0.1	0.0629 mM	0.72	----------	----------	RS6
10	PdO/MWCNT	0.095	1.41 mM	----	----------	----------	RS7
11	Microgel-1-Pd_9	0.1	2.15 mM	0.09	----------	----------	RS8
12	SPB-30-Pd_9	0.1	0.366 mM	0.264	----------	----------	RS8

References:

RS3. Y. Y. Shen, Y. Sun, L. N. Zhou, Y. J. Li and E. S. Yeung, *J. Mater. Chem. A*, 2014, **2**, 2977.

RS4. X. Lu, X. Bian, G. Nie, C. Zhang, C. Wang and Y. Wei, *J. Mater. Chem.*, 2012, **22**, 12723.

RS5. H. Li, S. Gan, D. Han, W. Ma, B. Cai, W. Zhang, Q. Zhanga and L. Niua, *J. Mater. Chem. A*, 2014, **2**, 3461.

RS6. J. Morere, M. J. Tenorio, M. J. Torralvo, C. J. Pando, A. R. Renuncio and A. Cabanas, *J. Supercrit. Fluids*, 2011, **56**, 213.

RS7. H. He and C. A. Gao *Molecules*, 2010, **15**, 4679.

RS8. Y. Mei, Y. Lu, F. Polzer, M. Ballauff and M. Drechsler, *Chem. Mater.*, 2007, **19**, 1062.