# Supporting Information

# Insight into Epitaxial Encapsulation of Pd Nanocatalysts in Oriented Metallporphyrin Network Thin Film for Tandem Catalysis

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## Experimental Section

### Materials and instrumentation

All reagents and solvents employed were commercially available and used as received without further purification unless otherwise stated. PXRD analysis was performed on a D8 Advance (Bruker) X-ray diffractometer using Cu-Kα radiation (λ = 0.1542 nm) in the 2θ range of 4–20° (thin film) and 5-70° (powder) with a scanning rate of 0.5° $min^{-1}$. In-plane XRD was performed on a SmartLab (Rigaku). Evaluation of data was done with Rigaku evaluation software JADE 5.0. SEM images for the morphology of thin films were measured using the JSM6700. The product components and the reaction conversions were monitored by GC-MS Varian-Agilent 4000GC-MS.

### Fabrication of PIZA-1 thin films

The thin film was fabricated using the following diluted ethanolic solutions: cobalt(II) acetate (1 mM) and TCPP (0.2 mM). The spray times were 15s and 25s for $Co(OAc)_2$ and TCPP solution, respectively. The interval between steps was 30s and pure ethanol was sprayed for 3s to remove residual reactants. A total of 30 growth cycles were used for in situ LPE layer-by-layer preparation of PIZA-1 thin film in this work.

### Synthesis of Pd-NCs@PIZA-1 thin film

The substrate was sprayed with cobalt acetate (1 mM), TCPP (0.2 mM) and $Pd[P(C_6H_5)_3]_4$ (0.2 mM) ethanol solutions sequentially. The spraying time was 15s,

25s and 10s for $Co(OAc)_2$, TCPP and $Pd[P(C_6H_5)_3]_4$ solution, respectively. There was waiting time for 30s between steps and each step was followed by a 3s spray step with pure ethanol to remove residual reactants. A total of 30 growth cycles were used for preparation of Pd-NCs@PIZA-1 thin film in this work.

**Synthesis of powder PIZA-1**

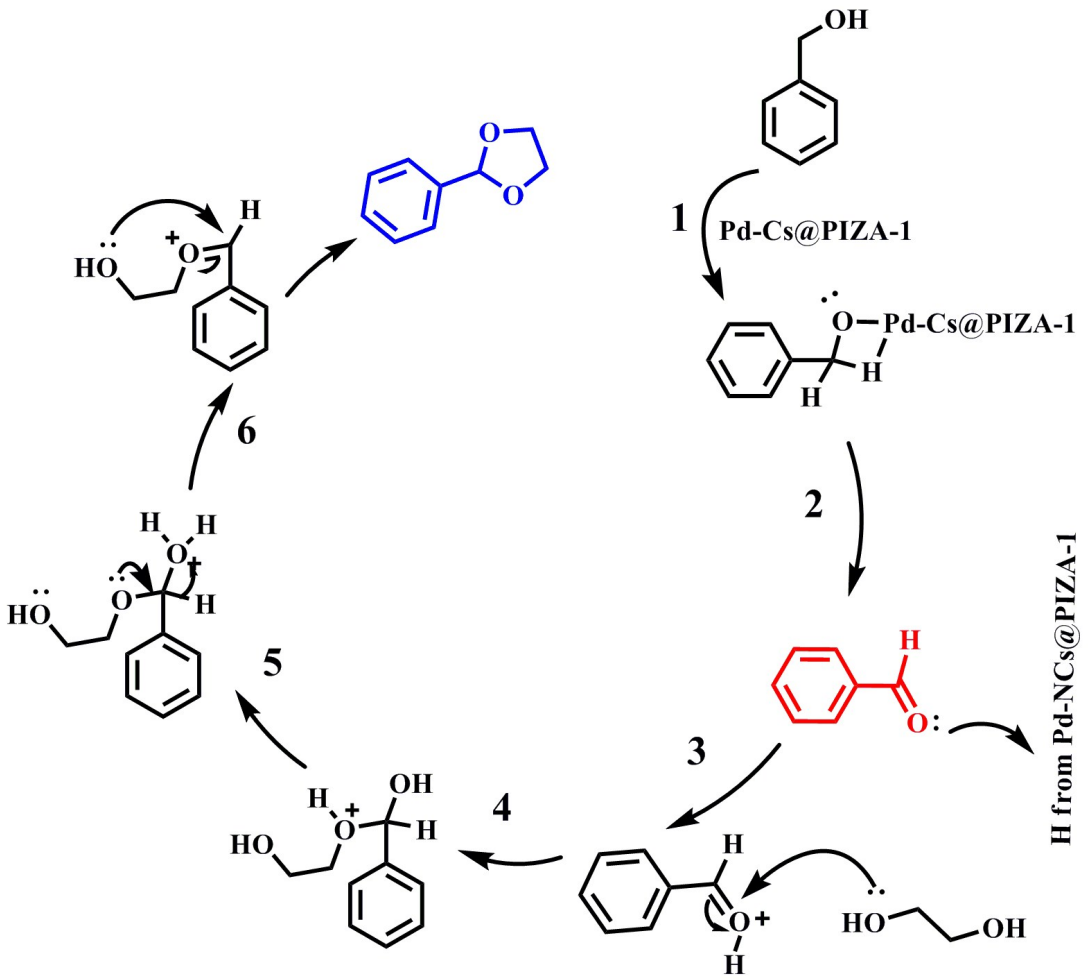
Powder PIZA-1 was synthesized by mixing 0.187 g (0.75 mmol) cobalt(II) acetate and 0.396 g(0.5 mmol) TCPP in 6 ml pure ethanol (drops of pyridine) in a sealed glass bottle. The reagents were mixed and dissolved in an ultrasonic bath for 30 min, followed by heating at 65 °C for 2 days and cooling to room temperature. The resulting powder was washed with pure ethanol and dried in nitrogen. By comparing with the simulated XRD of PIZA-1, the recorded XRD showed that powder PIZA-1 was synthesized.

**Procedure for Alcohol Oxidation**

Here, the tandem reaction of oxidation and acetalization of benzyl alcohol in a one pot manor was carried out at 80 °C in a 25 mL round-bottom flask fitted with a condenser. Pd-NCs@PIZA-1 thin film (catalyst) 1×1 cm size gold substrate was immersed in 10 mL of cyclohexane in the round-bottom flask. To the reaction mixture, benzyl alcohol (1 mmol) and ethylene glycol (100 μL 1.8 mmol) were slowly added. An oxygen balloon at the top of the condenser was fitted to supply oxygen for the reaction. The flask loaded in an oil bath was preheated to 80 °C. The reaction mixture was kept under reflux with magnetic stirring at 300 rpm for designated time. After the reaction, catalyst was separated and washed with ethanol several time, and the solvent

was evaporated. Then the product was dissolved in methanol and then analysed by GC-Mass. Authentic samples of reactants and respective products were used to verify the product formation. The products were identified by a GC-MS (SHIMADZU5050A) equipped with a HP-5ms capillary column (30 m ×0.25 mm × 0.25 μm).

The proposed reaction mechanism is shown in Scheme S1. Dehydrogenation oxidation of benzyl alcohol in step 1, starts with the coordination of oxygen on benzyl alcohol to palladium catalysts followed by hydride elimination, affording a oxidized product benzaldhyde in step 2 and a Pd hydride. This Pd hydride would react with molecular oxygen to generate $H_2O$ and Pd specie. The carboxyl group of benzaldehyde in step 3 accepts a proton from porphyrin-based MOF and becomes protonated. Due to protonation step makes the carbonyl group highly electrophillic in nature, so that the ethylene glycol is a weak nucleophile which can be attacked easily by its hydroxyl group on the highly polarized carbonyl carbon resulted *via* a hemiacetal process (in step 4).[22, 42] Then, the proton transferring (in step 5) makes the elimination of water by the push of lone pair of oxygen atom from ethylene glycol, resulting in an oxonium ion. The remaining hydroxyl group of ethylene glycol attacks on the oxonium specie gives a cyclic acetal product. After that, removing of proton give desired product (in step 6).




**Scheme S1**. The proposed mechanism of tandem reaction with Pd-Cs@PIZA-1 thin film catalyst.

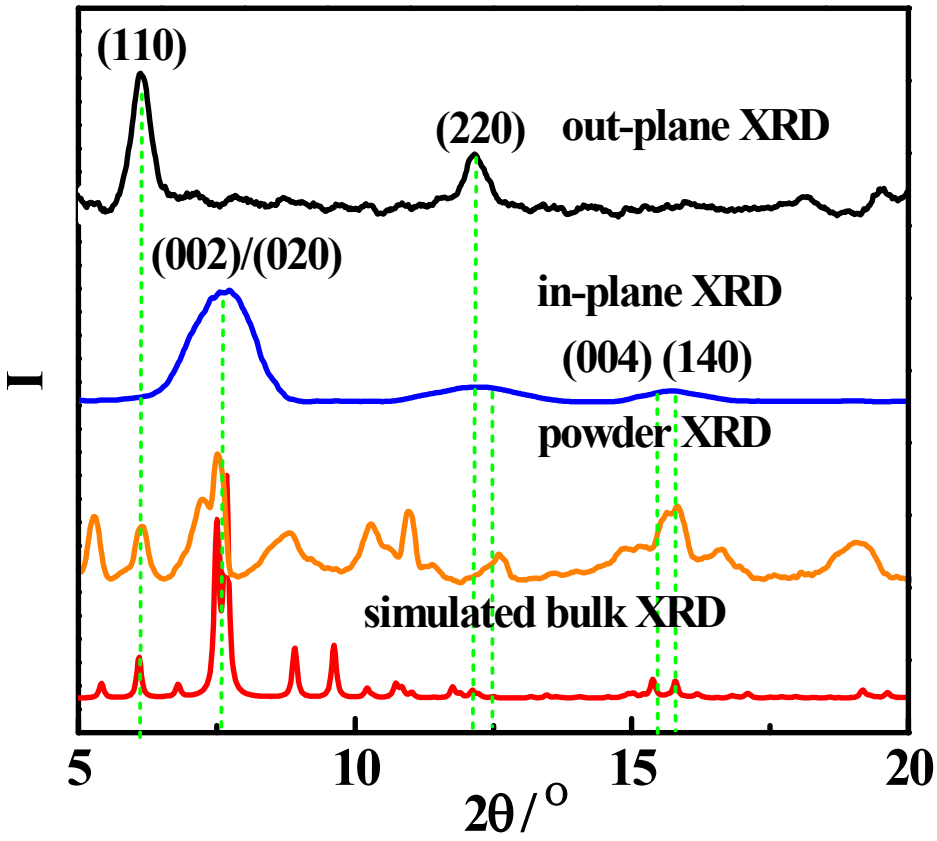



**Figure S1**. Out- and in-plane XRD of PIZA-1 thin film on MUD SAM substrate, powder PIZA-1 and simulated XRD of bulk PIZA-1.

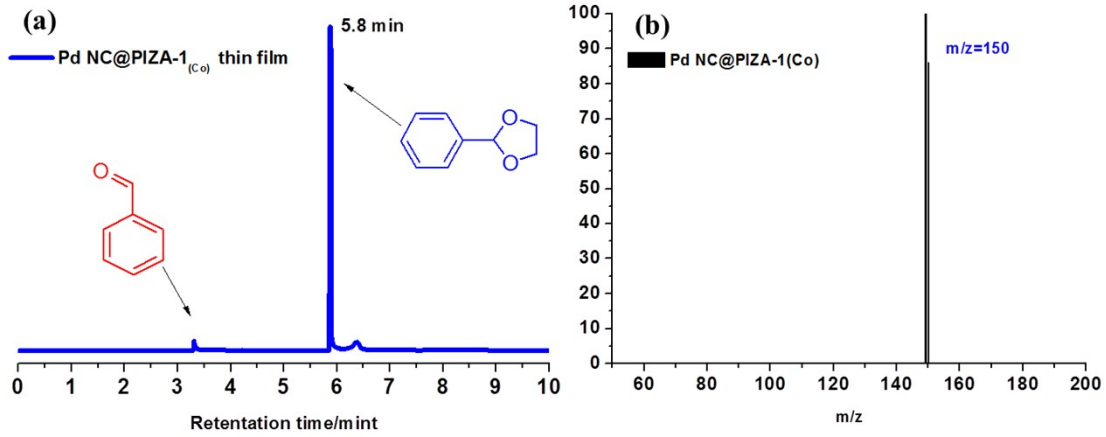



**Figure S2**. GC-MS analysis of benzyl alcohol oxidation and acetalization catalyzed by Pd-NCs@PIZA-$1_{(Co)}$ thin film (80°C, 8h, conversion, 85% ) which further confirm by mass spectra show m/z 150.

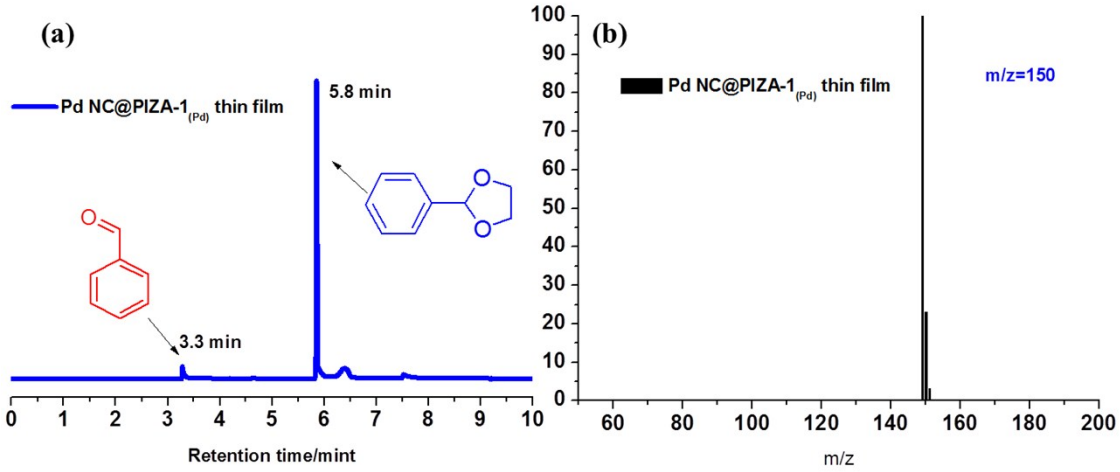



**Figure S3**. GC-MS analysis of benzyl alcohol oxidation and acetalization catalyzed by Pd-NCs@PIZA-$1_{(Pd)}$ thin film (80°C, 8h, conversion, 71.9% ) which further confirm by mass spectra show m/z 150.

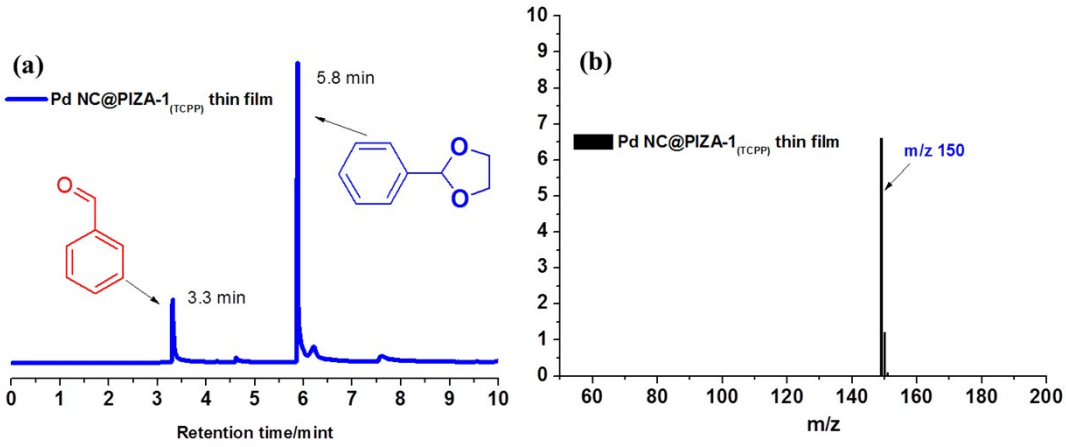



**Figure S4**. GC-MS analysis of benzyl alcohol oxidation and acetalization catalyzed by Pd-NCs@PIZA-$1_{(TCPP)}$ thin film (80°C, 8h, conversion, 70.0% ) which further confirm by mass spectra show m/z 150.

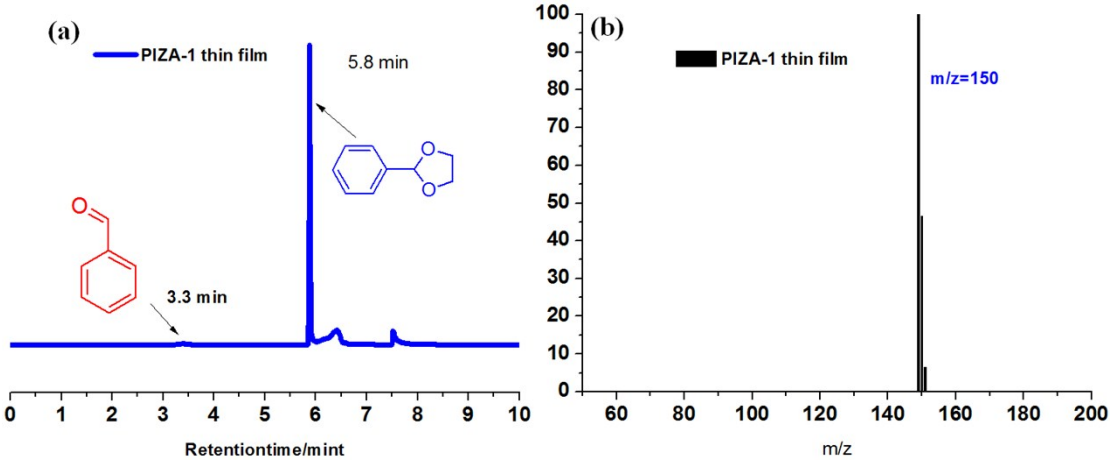



**Figure S5**. GC-MS analysis of benzyl alcohol oxidation and acetalization catalyzed by PIZA-1 thin film (80°C, 8h, conversion, 93.0% ) which further confirm by mass spectra show m/z 150.

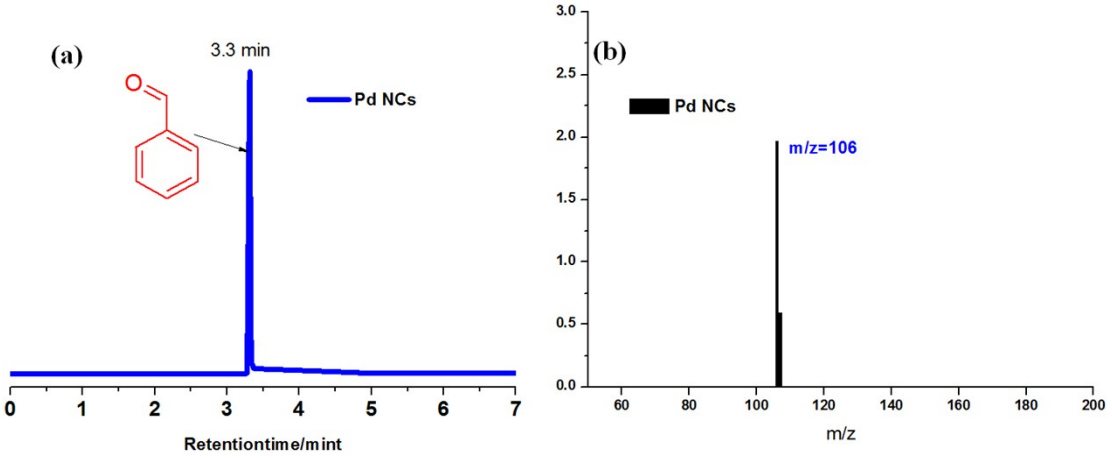



**Figure S6**. GC-MS analysis of benzyl alcohol oxidation catalyzed by Pd-NCs (80°C, 8h, conversion, 100.0 % ) which further confirm by mass spectra show m/z 106.

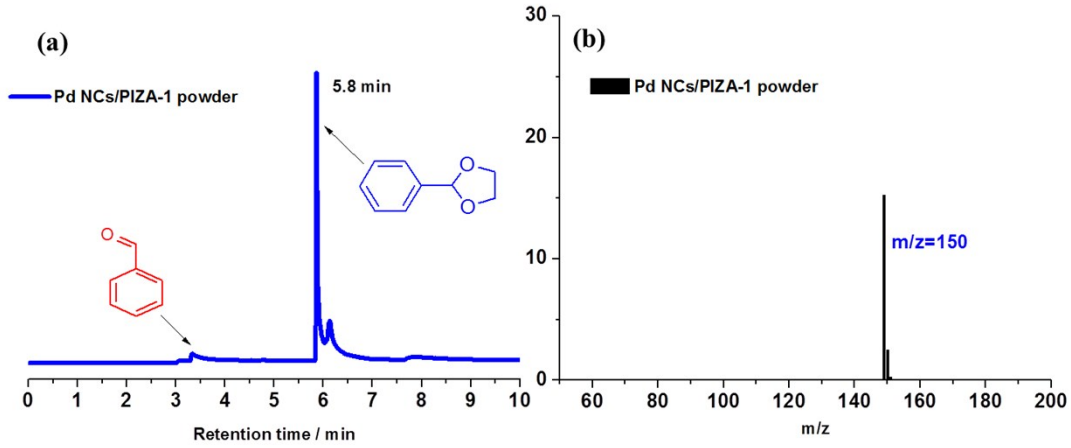



**Figure S7**. GC-MS analysis of benzyl alcohol oxidation and acetalization catalyzed by Pd-NCs mixed with PIZA-1 powder (80°C, 8h, conversion, 55.3 % ) which further confirm by mass spectra show m/z 150.

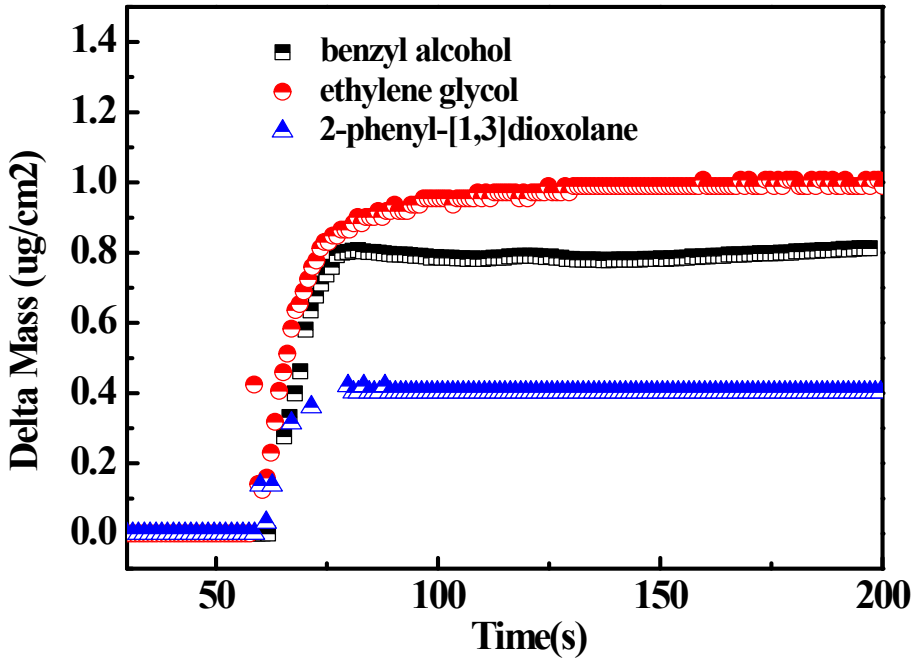



**Figure S8**. The uptake of benzyl alcohol, ethylene glycol and 2-(phenyl)-[1,3]-dioxolane on PIZA-1 thin film.

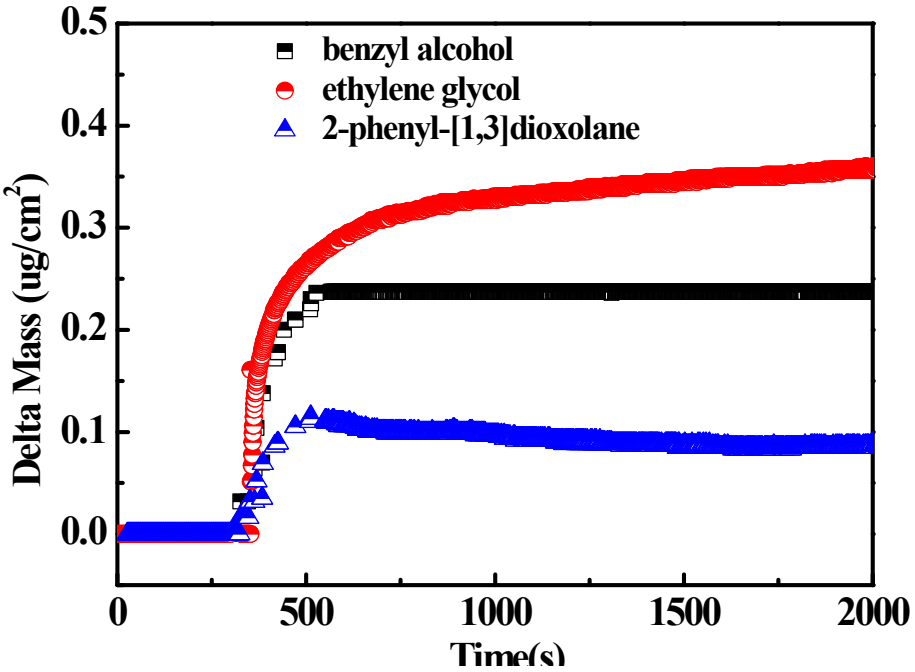



**Figure S9**. The uptake of benzyl alcohol, ethylene glycol and 2-(phenyl)-[1,3]-dioxolane on Pd-NCs@PIZA-1 thin film.

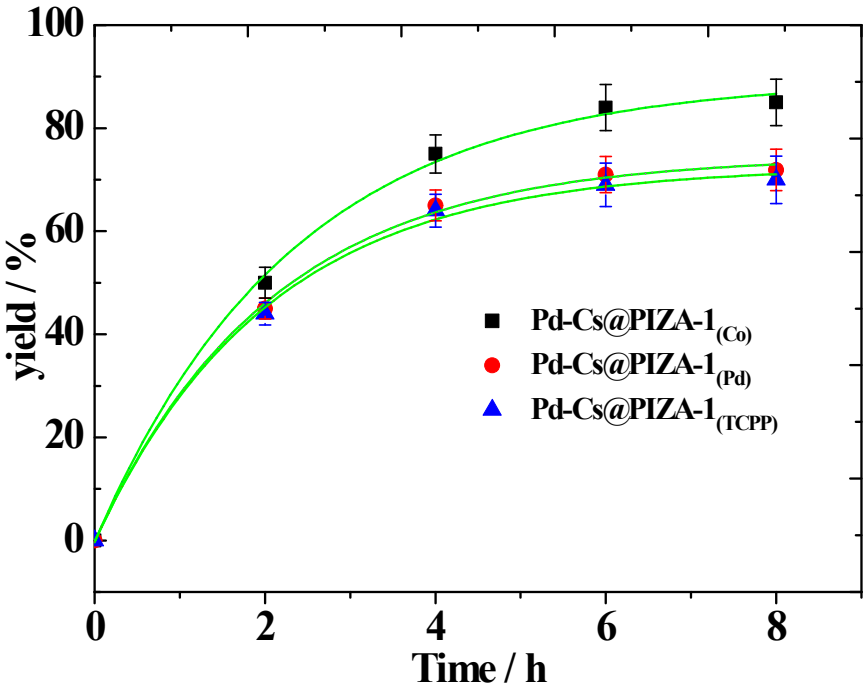
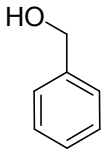
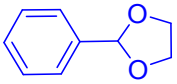
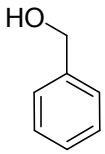
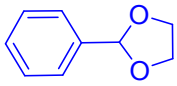
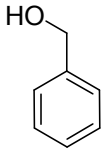
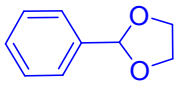
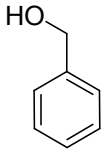
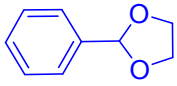



**Figure S10**. The yield of Pd-Cs@PIZA-$1_{(Co)}$, Pd-Cs@PIZA-$1_{(Pd)}$ and Pd-Cs@PIZA-$1_{(TCPP)}$ after catalysts reaction with 2, 4, 6 and 8 h, respectively. The related rate constant of the Pd-Cs@PIZA-$1_{(Co)}$, Pd-Cs@PIZA-$1_{(Pd)}$, and Pd-Cs@PIZA-$1_{(TCPP)}$ were ~233, 208 and 204, respectively.

**Table S1. Recycling test with Pd-NCs@PIZA-1$_{(Pd)}$ thin film catalyst.**

| Entry | sample | substrate | Product | t(h) | GC-MS Yield (%) |
|---|---|---|---|---|---|
| 1 | Pd-NCs@PIZA-1$_{(Pd)}$ thin film |  |  | 8 | 71.9 |
| 2 | Pd-NCs@PIZA-1$_{(Pd)}$ thin film |  |  | 8 | 71.0 |
| 3 | Pd-NCs@PIZA-1$_{(Pd)}$ thin film |  |  | 8 | 67.2 |
| 4 | Pd-NCs@PIZA-1$_{(Pd)}$ thin film |  |  | 8 | 65.5 |