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In situ confinement of ultra-small metal nanoparticles in redox-active Zirconium MOFs for catalysis

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1. Synthesis of H₄TCPA linker:

N,N,N',N'-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine (H₄TCPA) was synthesized according to the literature with some modifications^[1,2]:

1.1. Synthesis of 4,4',4'',4'''-(1,4-phenylenebis(azanetriyl)) tetrabenzonitrile

A mixture of 2.80 g (0.04 mol) of sodium hydride and 100 mL of anhydrous DMF was stirred for about 0.5 h at room temperature. To this mixture, 1.08 g (0.01 mol) of p-phenylenediamine and 9.68 g (0.04 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 120 °C for 30 h under nitrogen and then precipitated into 200 mL of cold water. The products were filtered and purified by flash chromatography to give pale yellowish solid 2.51 g (yield: 64 %). ¹H NMR (CDCl₃): δ = 6.84 (s, 4H), 7.04 (d, 8H), 7.62 (d, 8H).

1.2. Synthesis of H₄TCPA

3.92 g (0.01 mmol) of 4,4',4'',4'''-(1,4-phenylenebis(azanetriyl)) tetrabenzonitrile and 7.8 g of potassium hydroxide were mixed in a 100 mL CH₃CH₂OH/H₂O (1:1) solution. The mixture was heated to reflux for 20 hours until no further ammonia was generated. The solution was cooled, and the pH value was adjusted by dilute hydrochloric acid to near 3. The yellowish precipitate formed was collected by filtration, washed thoroughly with water. Recrystallization from acetic acid gave pale yellow crystals 4.10 g. (yield: 87.6 %). ¹H NMR (300 MHz, *d*⁶-DMSO) δ = 7.08 (s, 4 H), 7.12 (d, 8 H), 7.95 (d, 8 H).

2. Synthesis of compounds 1 and 2

2.1 Synthesis of compound 1

ZrCl₄ (20 mg), H₄TCPA (10 mg), and benzoic acid (400 mg) in 2 mL of DMF were ultrasonically dissolved in a 4 mL glass scintillation vial. The mixture was heated in an oven to 120 °C for 36 h. After cooling down to room temperature, light-yellow crystals were harvested by filtration (7 mg, 70% yield).

2.2 Synthesis of compound 2

ZrCl₄ (20 mg), H₄TCPA (10 mg), and 0.1 mL TFA in 3 mL of DMF were ultrasonically dissolved in a 4 mL glass scintillation vial. The mixture was heated in an oven to 120 °C for 36 h. After cooling down to room temperature, yellow powders were harvested by filtration (6 mg, 70% yield).

2.3 Synthesis of Eu-mof

Eu(NO₃)₃·6H₂O (5 mg), H₄TCPA (1 mg), 2-fluorobenzoic acid (100 mg) were

dissolved into a mixture solution of DMF/H₂O (V:V = 1:1, 1.1 mL) in a 10 mL vial, which was then sealed, heated in a preheated oven at 120 °C for 24 h. After cooling to room temperature, the colorless crystals were collected and washed with DMF.

3. Synthesis of Pd NPs@1 and Pd NPs@2

Typically, the prepared compound **1** were immersed in an acetonitrile solution of Pd(NO₃)₂ (1.0×10^{-3} M) for 12h at room temperature in the dark. The brown solid of Pd NPs@**1** resulted, which was filtered off, washed with fresh MeCN for three times to remove the metal salts, and dried in the air. Pd NPs@**2** were synthesized by a similar procedure, except that compound **2** was used.

4. General Characterizations:

Table S1. Crystal data and structure refinements.

	Compound 1	Eu-MOF
CCDC	2294100	2359884
Formula	Zr ₆ C ₆₈ H ₅₆ N ₄ O ₃₂	Eu ₆ C _{68.5} H ₄₀ F ₈ N ₄ O _{24.5}
Compositions	Zr ₆ (μ ₃ -O) ₄ (TCPA) ₂ (OH) ₄ (H ₂ O) ₄	Eu ₆ (μ ₃ -F) ₈ (TCPA) ₂ (HCOO) ₄ (H ₂ O) ₄
Formula weight	1972.36	2374.80
Color/Shape	colorless	colorless
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Fmmm</i>	<i>Fmmm</i>
<i>a</i> (Å)	17.936 (2)	19.893 (3)
<i>b</i> (Å)	30.464 (4)	30.475 (4)
<i>c</i> (Å)	31.068 (4)	31.958 (5)
<i>α</i> (°)	90.00	90.00
<i>β</i> (°)	90.00	90.00
<i>γ</i> (°)	90.00	90.00
<i>V</i> (Å ³)	16975 (3)	19375 (5)
<i>Z</i>	4	4
Wavelength (Å)	0.71073 (MoK _α)	0.71073 (MoK _α)
<i>d</i> _{calcd.} (g/cm ³)	0.772	0.814
<i>μ</i> (mm ⁻¹)	0.395	1.951
<i>θ</i> _{max} [deg]	23.4	25.026
Completeness	95.2 %	99.6 %
Collected reflections	42911	98316
Unique reflections	3183	4599
Parameters	135	144
Restraints	306	330
<i>R</i> _{int}	0.454	0.1105
<i>R</i> ₁ (all data)	0.1931	0.1842
<i>wR</i> ₂ (all data)	0.3014	0.3461
GOF on <i>F</i> ²	1.053	1.118
$\Delta\rho_{\max}/\Delta\rho_{\min}$ [e ⁻ Å ⁻³]	1.23 / -1.08	3.50/-3.29

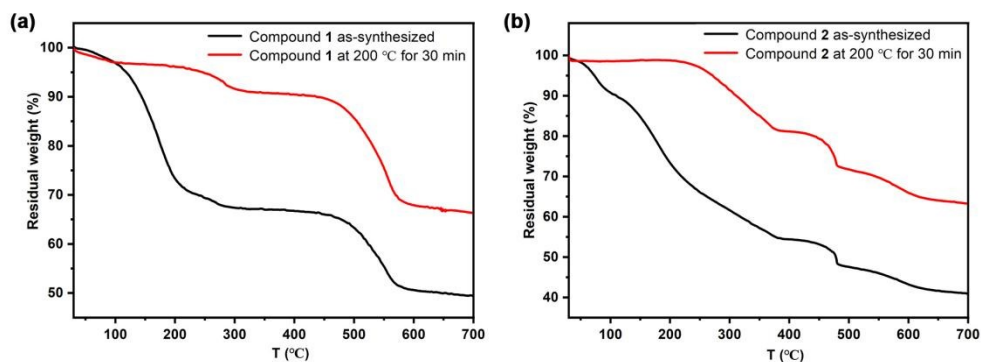


Figure S1. The TGA plots of compound 1 (a) and compound 2 (b).

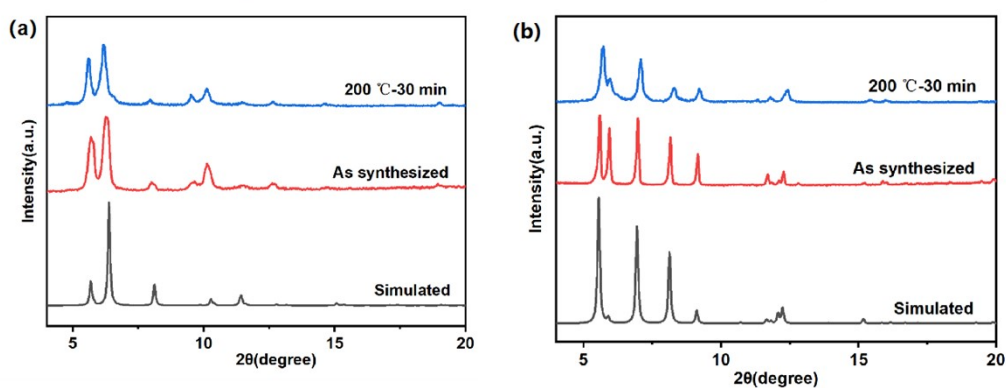


Figure S2. The PXRD patterns of compound 1 (a) and 2 (b) after heating at 200 °C for 30 min

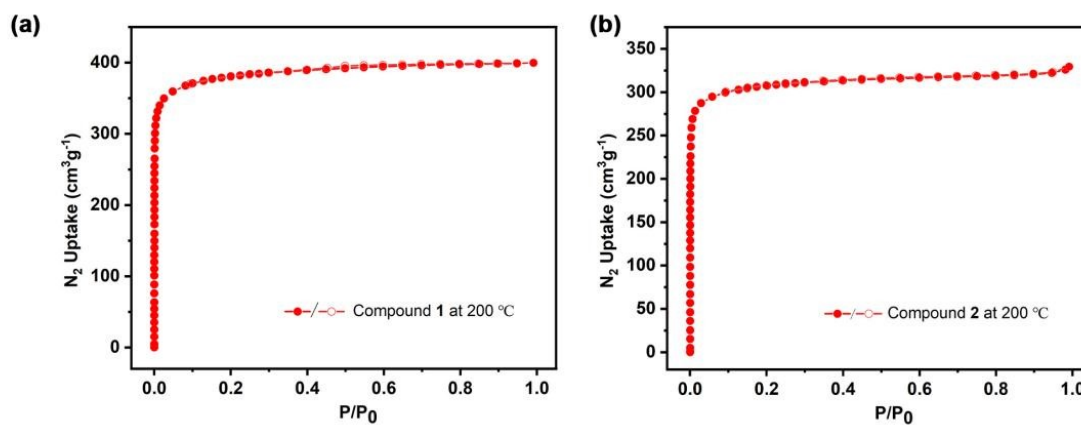


Figure S3. The N₂ adsorption-desorption isotherms of compound 1 (a) and 2 (b) after heating at 200 °C for 30 min

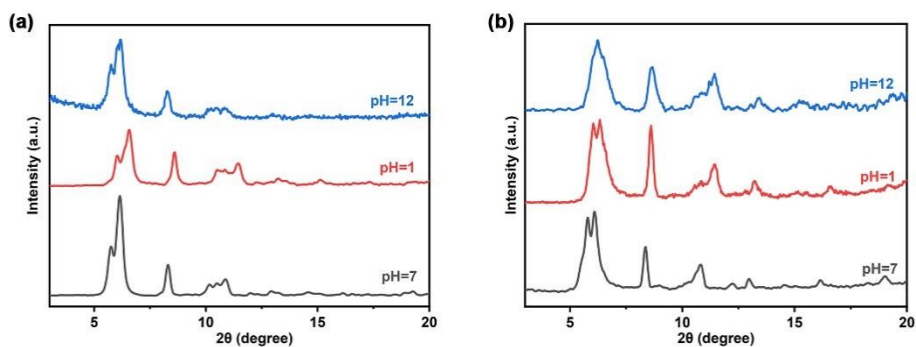


Figure S4. The chemical stabilities of compounds **1** (a) and **2** (b) were confirmed by comparing the PXRD patterns before and after immersion in aqueous solutions with various pH values for 24 h.

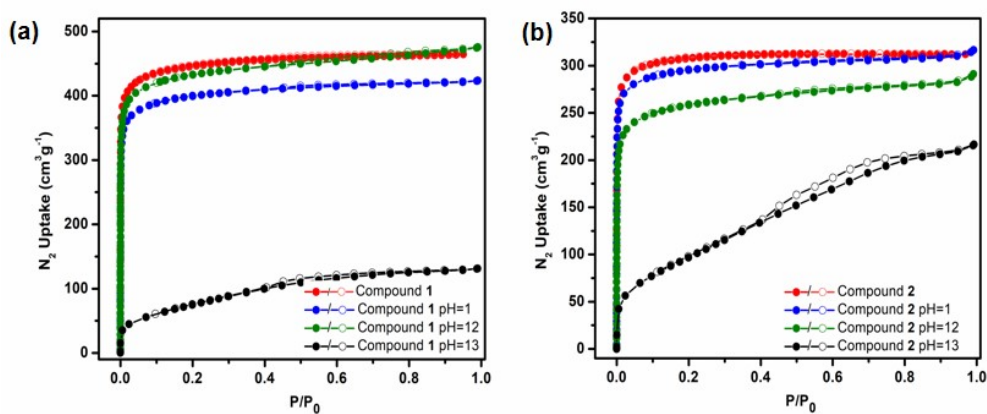


Figure S5. the N_2 adsorption-desorption isotherms of compound **1** and **2** in aqueous solutions with various pH values for 24h

5. Redox Activity:

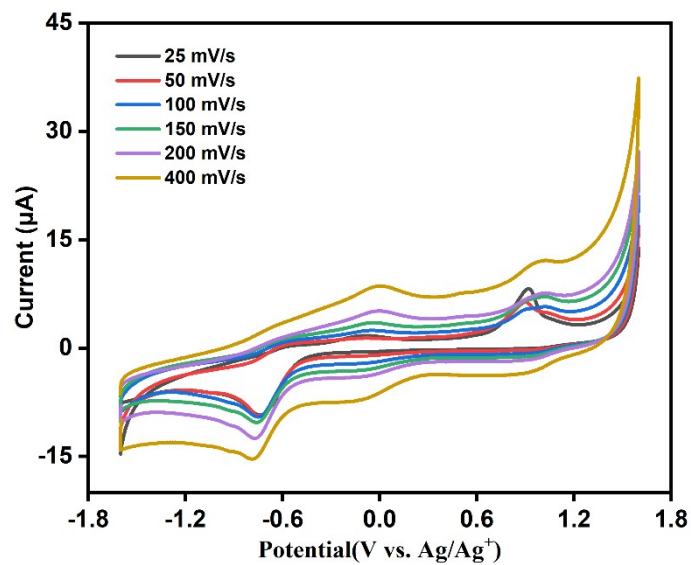


Figure S6. Solid state cyclic voltammogram of H₄TCPA swept anodically at scan rates of 25-400 mV/s.

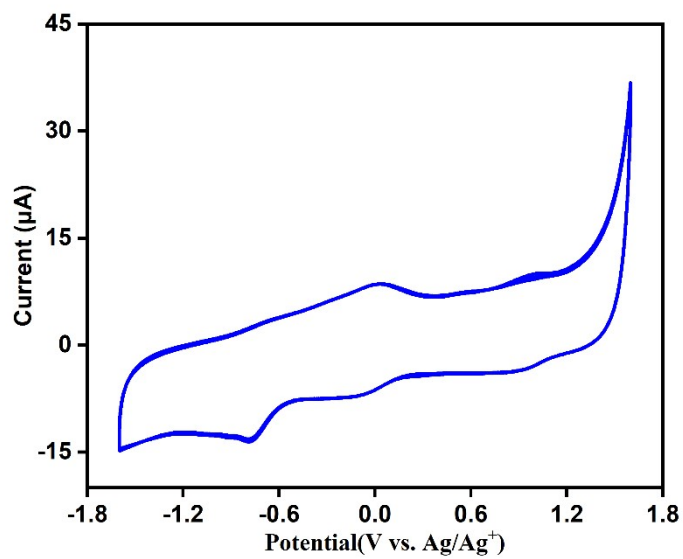


Figure S7. Solid state CV of H₄TCPA upon cycling anodically at 400 mV/s three times.

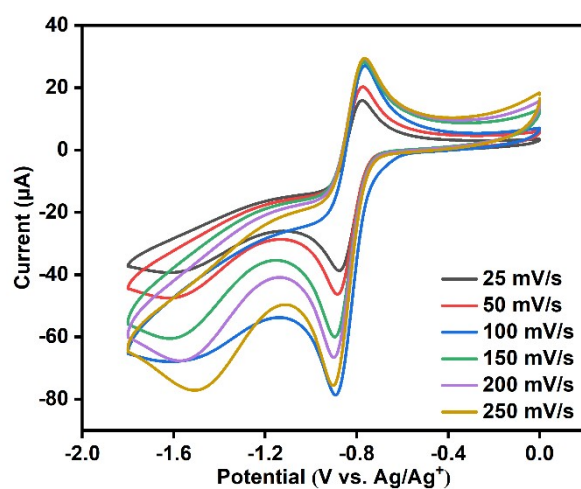


Figure S8. Solid state cyclic voltammogram of compound **1** swept anodically at scan rates of 25-250 mV/s.

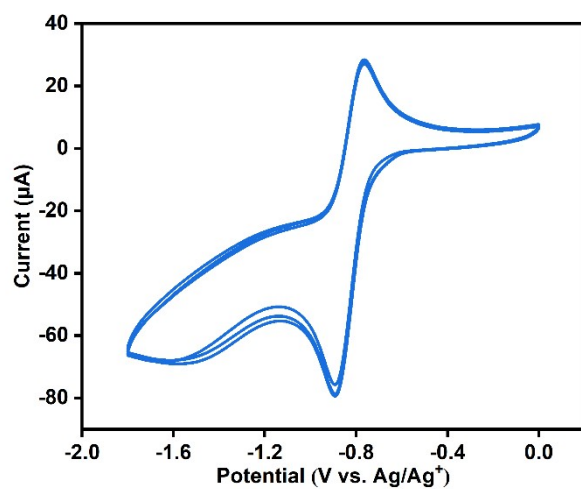


Figure S9. Solid state CV of compound **1** upon cycling anodically at 100 mV/s three times.

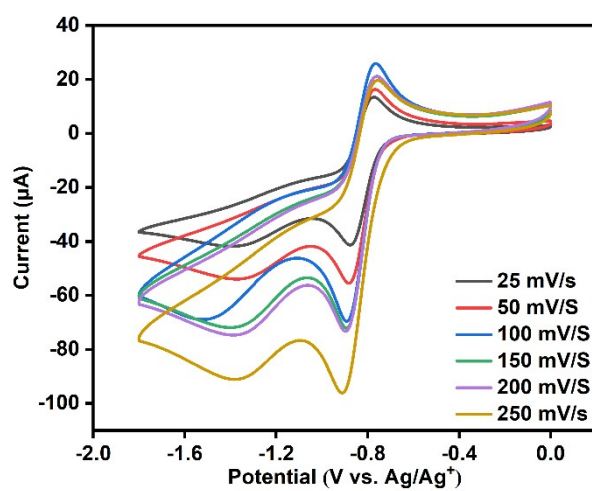


Figure S10. Solid state cyclic voltammogram of compound **2** swept anodically at scan rates of 25-250 mV/s.

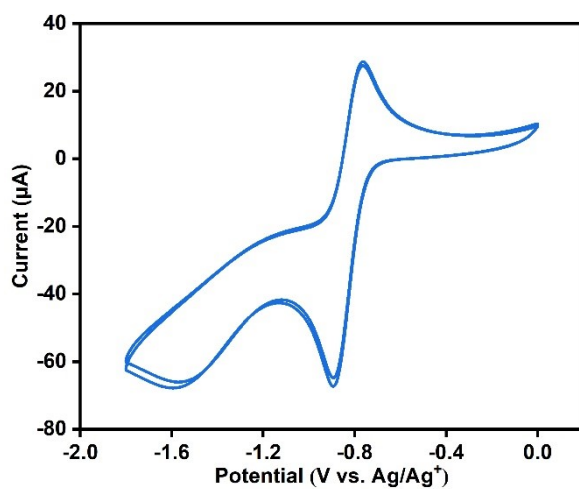


Figure S11. Solid state CV of compound **2** upon cycling anodically at 100 mV/s three times.

6. General Characterizations of Pd@MOFs:

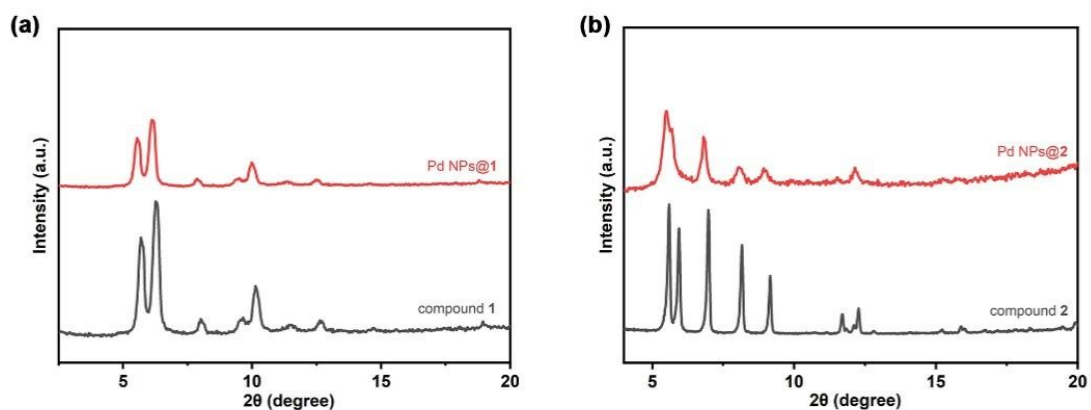


Figure S12. X-ray powder diffraction patterns for Pd NPs@1, compounds 1 (a) and Pd NPs@2, compounds 2 (b).

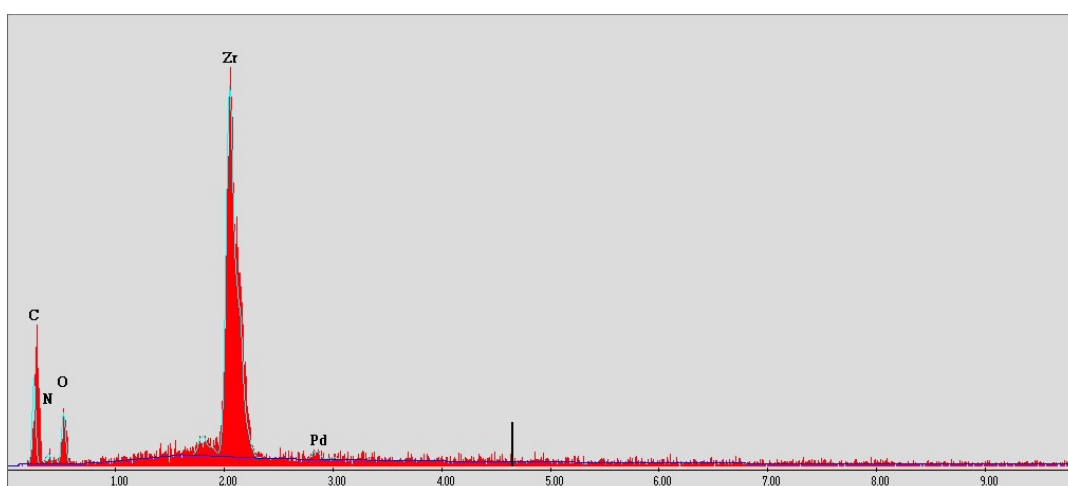


Figure S13. EDS of Pd NPs@1.

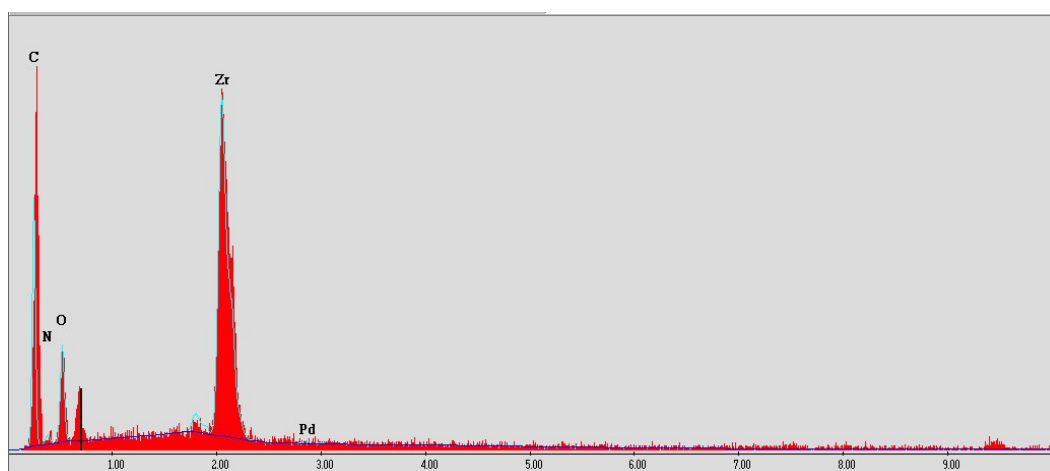


Figure S14. EDS of Pd NPs@2.

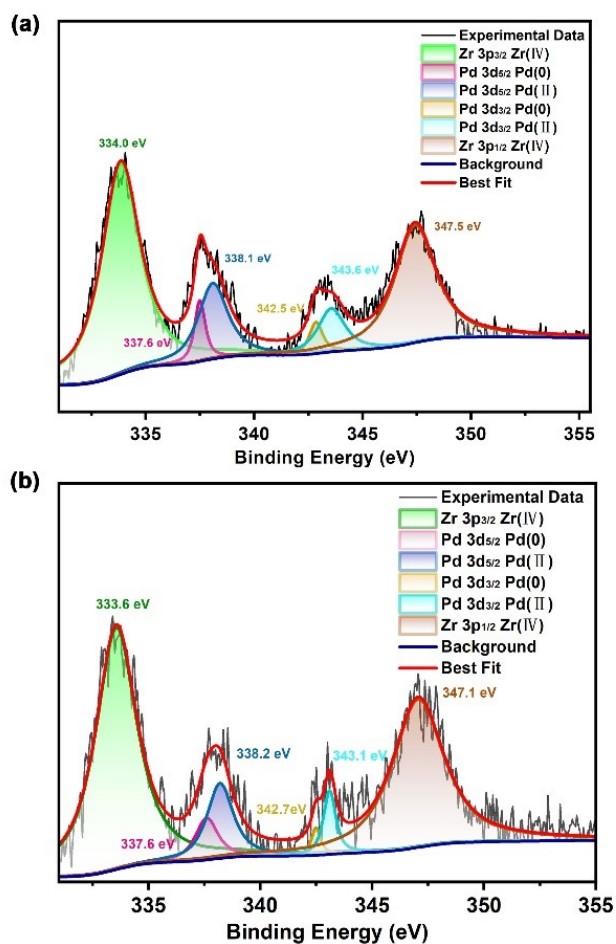


Figure S15. X-ray photoelectron spectra of Pd NPs@1 (a) and Pd NPs@2 (b).

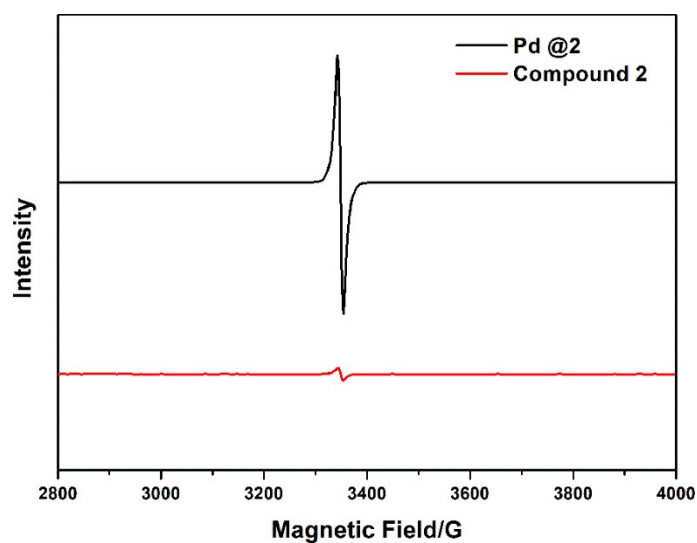


Figure S16. The solid state EPR spectra of compound 2 and Pd@2 at 110 K.

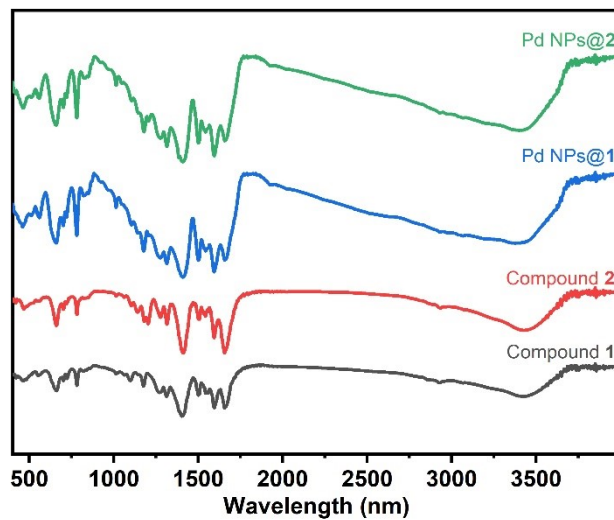


Figure S17. The IR spectra for compound 1, compound 2, Pd NPs@1, Pd NPs@2.

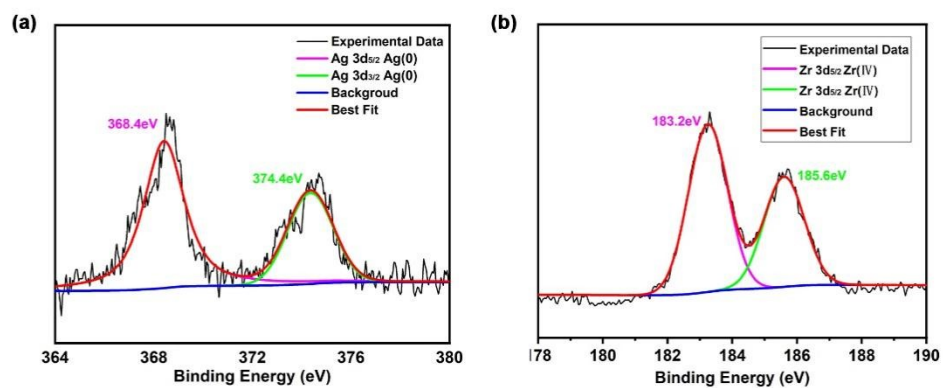


Figure S18. X-ray photoelectron spectra of Ag NPs@1.

7. Catalytic Activity:

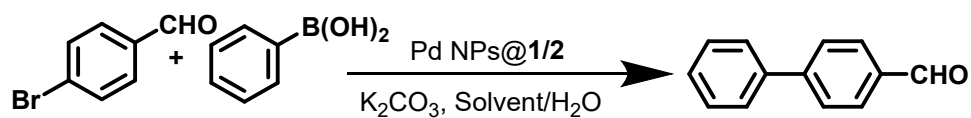


Figure S19. 4-bromobenzaldehyde (0.5 mmol), phenylboronic (0.6 mmol), K₂CO₃ (1.0 mmol) Pd NPs@1/2(5.0 mg) in above organic solvents (2.0 mL) and H₂O (0.5 mL) for 2 h at 100°C

Table S2. Screening conditions of Pd NPs@1 for the Suzuki-Miyaura coupling reaction.

Entry	Solvent	Time (h)	Conversion (%)
1	DMF	2	99
2	THF	2	54
3	Toluene	2	48
4	CH ₃ CN	2	91

Table S3. Screening conditions of Pd NPs@2 for the Suzuki-Miyaura coupling reaction

Entry	Solvent	Time (h)	Conversion (%)
1	DMF	2	99
2	THF	2	67
3	Toluene	2	70
4	CH ₃ CN	2	89

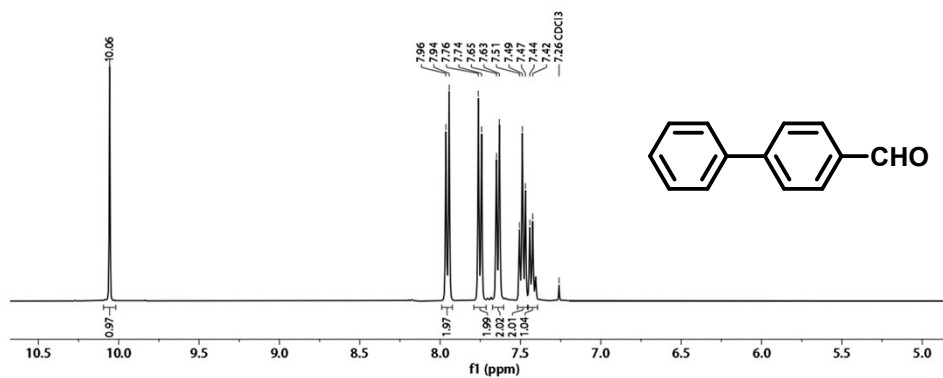


Figure S20. ^1H NMR (400 MHz, Chloroform-d) of [1,1'-biphenyl]-4-carboxaldehyde: δ 10.06 (s, 1H), 7.95 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 7.0$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.43 (d, $J = 7.2$ Hz, 1H).

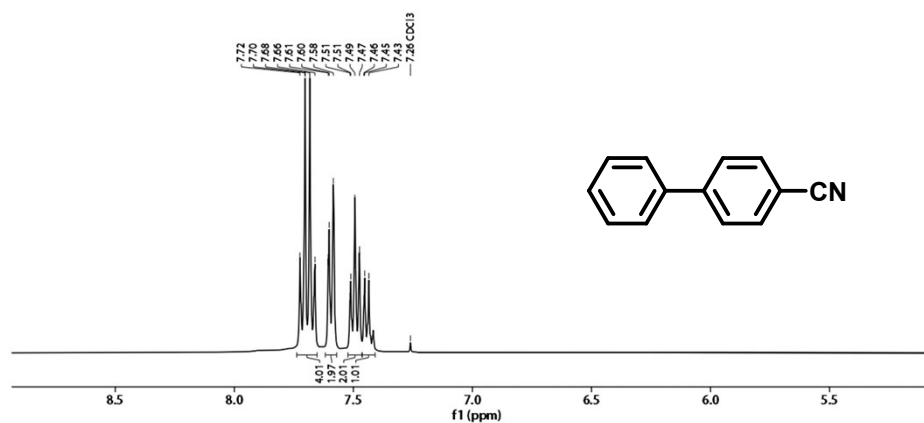


Figure S21. ^1H NMR (400 MHz, Chloroform-d) of [1,1'-biphenyl]-4-carbonitrile: δ 7.69 (q, $J = 8.7$ Hz, 4H), 7.62 – 7.57 (m, 2H), 7.49 (t, $J = 7.3$ Hz, 2H), 7.46 – 7.41 (m, 1H).

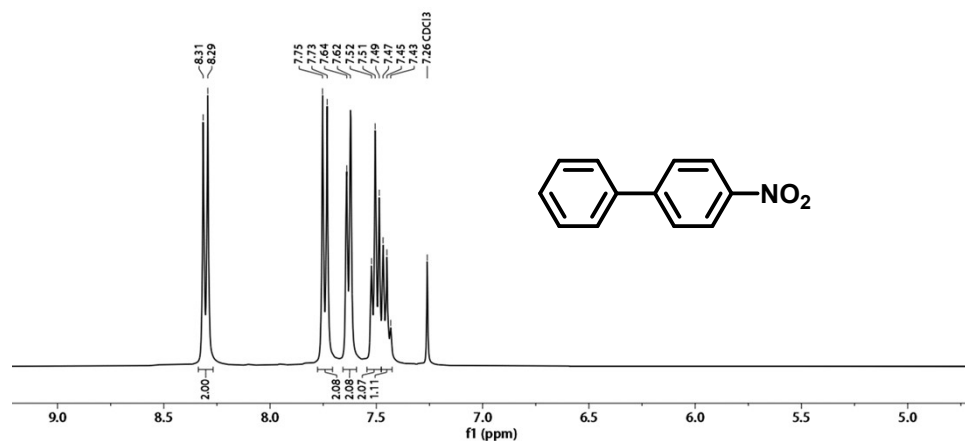


Figure S22. ^1H NMR (400 MHz, Chloroform-d) of 4-nitro-1,1'-biphenyl: δ 8.30 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 6.6 Hz, 2H), 7.50 (t, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H).

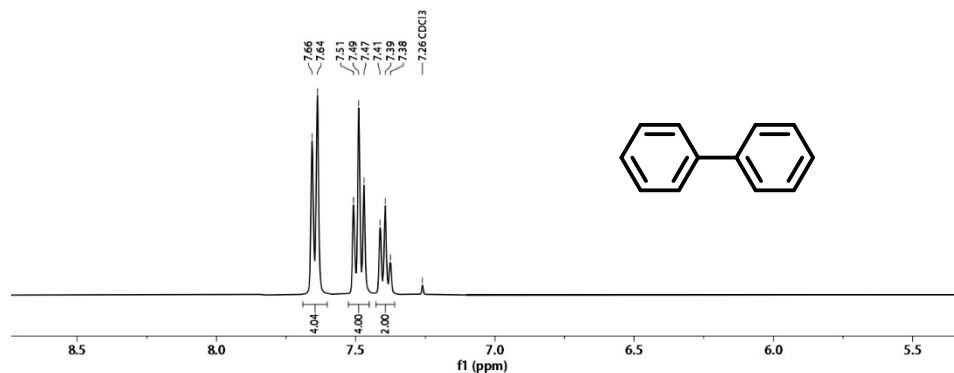


Figure S23. ^1H NMR (400 MHz, Chloroform-d) of 1,1'-biphenyl: δ 7.65 (d, J = 7.6 Hz, 4H), 7.49 (qt, J = 10.1, 7.6, 0.0 Hz, 4H), 7.39 (t, J = 7.4 Hz, 2H).

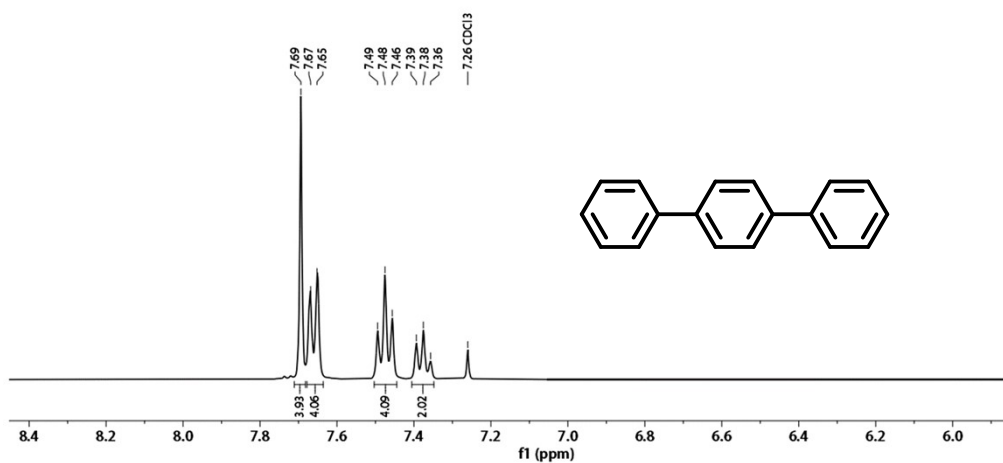


Figure S24. ^1H NMR (400 MHz, Chloroform-d) of 1,1':4',1''-terphenyl: δ 7.69 (s, 4H), 7.66 (d, J = 6.7 Hz, 4H), 7.48 (t, J = 7.6 Hz, 4H), 7.38 (t, J = 7.4 Hz, 2H).

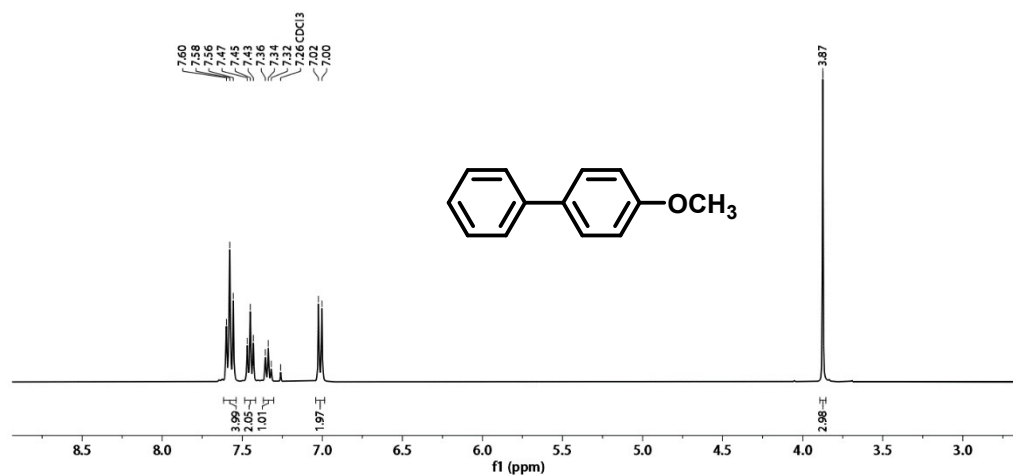


Figure S25. ^1H NMR (400 MHz, Chloroform- d) of 4-methoxy-1,1'-biphenyl: δ 7.58 (t, $J = 8.5$ Hz, 4H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H).

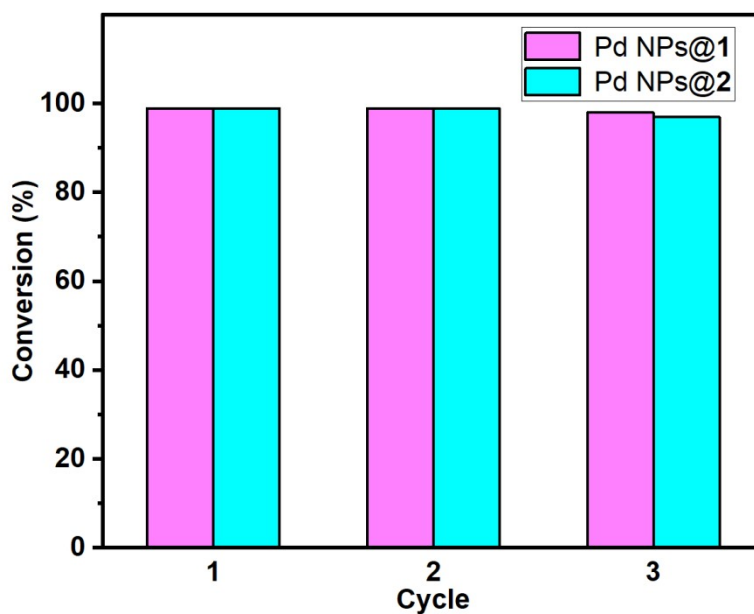


Figure S26. The yield of Suzuki-Miyaura coupling reaction product after three-time catalytic cycles using 4-bromobenzaldehyde as substrate.

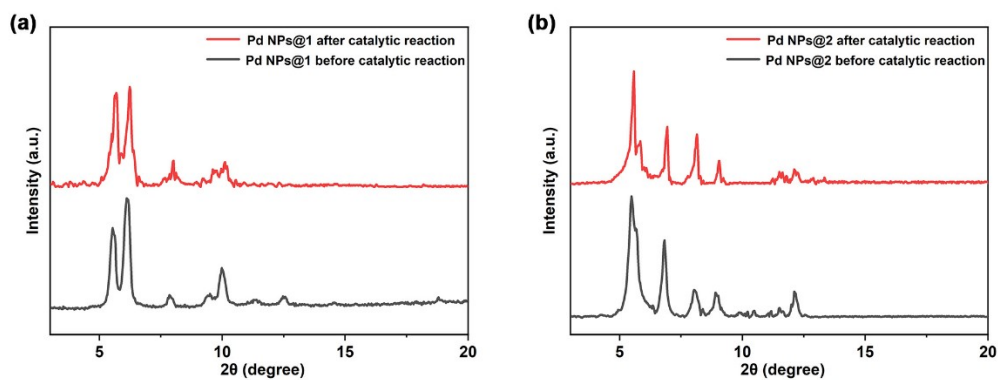


Figure S27. X-ray powder diffraction patterns for Pd NPs@1 (a) and Pd NPs@2 (b) before and after Suzuki-Miyaura coupling reactions using 4-bromobenzaldehyde as substrate.

Reference

- [1] Sun D., Ke Y.; Mattox T. M., Ooro B. A., Zhou H. C., *Chem. Commun. (Camb.)*, 2005, 5447-5449.
- [2] Sun D., Collins D. J., Ke Y., Zuo J. L., Zhou H. C., *Chem. - Eur. J.*, 2006, 12, 3768-3776.