Supplementary Information

Zirconium Metal–Organic Frameworks Incorporating Tetrathiafulvalene Linkers: Robust and Redox-Active Matrices for *insitu* Confinement of Metal Nanoparticles

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Materials and Instrumentation

All the reagents and solvents were commercially available and used as received. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. FT-IR data were recorded on a Vector27 Bruker Spectrophotometer with KBr pellets in the 4000 – 400 cm⁻¹ region. TGA data of compounds 1, 2, $I_3^-@1$ and $I_3^-@2$ were obtained on a STA 449C thermal analysis system with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. TGA data of MNPs@1 and MNPs@2 were obtained on a STA 449C thermal analysis system with a heating rate of 10 °C min⁻¹ under air atmosphere. The PXRD data were collected with a scan speed of 5 s \cdot deg⁻¹ on a Bruker Advance D8 (40 kV, 40 mA) diffractometer with Cu radiation (λ = 1.54056 Å) at room temperature. Calculated PXRD patterns were generated using Mercury 3.0. Electron paramagnetic resonance (EPR) spectra were obtained by using a Bruker EMX-10/12 variabletemperature apparatus at 110 K. Gas sorption measurements were conducted using a Micrometritics ASAP 2020 system. The SEM images were recorded on Hitachi S-3400N II and with EX-250 energy-dispersive X-ray micro analyzer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired on a JEOL JEM 2100 microscope (200 kV). The samples were prepared by casting powder sample dispersions in ethanol on carbon-coated copper grids. Precise elemental concentrations of Ag, Pd, Au, and Zr were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Optima 5300DV plasma ion spectrum mass spectrometer, for which the samples were prepared by dissolving NPs in H_2O_2/HNO_3 (1:1, v/v) with controlled concentrations. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000 VersaProbe X-ray photoelectron spectrometer using standard and monochromatic Al K_a radiation. The binding energies from the spectra were calibrated against the C 1s peak located at 284.6 eV. Solid state cyclic voltammetry measurements were performed in TBAPF₆/CH₃CN electrolyte using a BASi Epsilon electrochemical analyser and three electrode system. Argon was bubbled through solutions of 0.1 M TBAPF₆ dissolved in distilled CH₃CN. The CVs were recorded using a glassy carbon working electrode (1.5 mm diameter), a platinum wire auxiliary electrode and an Ag/Ag⁺ wire quasi-reference electrode. The sample was

mounted on the glassy carbon working electrode by dipping the electrode into a paste made of the powder sample in CH_3CN . Ferrocene was added as an internal standard upon completion of each experiment. All potentials are reported in mV versus Fc/Fc^+ couple.

X-Ray Crystallographic Analysis

Crystal structure determination and Rietveld refinement by powder X-ray diffraction:

We applied Ab initio powder X-ray diffraction crystal structure determination and Rietveld refinement for compound **1**.

The Powder X-ray Diffraction of compound 1 was measured on PANalytical X'Pert Powder X-ray powder diffractometer operated at a voltage of 60 kV and current of 55 mA with CuK α radiation ($\lambda = 1.5418$ Å) from 2.5 to 40° with step of 0.02°. The background was subtracted before crystal structure determination. Peak hunting, indexing, cell parameter determination refinement and the space group determination was conducted by the program of CMPR and EXPO2014, The initial structure was solved by the combination simulated Annealing + direct space method by program of EXPO2014. The final structure refinement was conducted by the Fullpro program. The observed and refined profiles shows good agreement with $R_p = 3.69\%$, $R_{wp}=4.15\%$, $\chi^2=1.33$.

Single Crystal Structure Studies. Data of TTFTB-OEt was collected on a Bruker D8 Venture diffractometer outfitted with a PHOTON-100 CMOS detector using monochromatic microfocus Mo- K_{α} radiation ($\lambda = 0.71073$ Å) that was operated at 50 kV and 40 mA at 153 K by a chilled nitrogen flow controlled by a KRYOFLEX II low temperature attachment. Data of 2, $I_3^-@2$, Ag NPs@2, and Au NPs@2 were collected on a MarCCD mx300 in the National Center for Protein Sciences Shanghai at the Shanghai Synchrotron Radiation Facility at 100 K. The diffraction data of 2, I₃⁻@2, Ag NPs@2, and Au NPs@2 were transformed by APEX3 (The file type of the diffraction pictures was changed from name.mccd to name.sfrm). The raw data collection and reduction were done using APEX3 software.¹ Adsorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.² Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of TTFTB⁴⁻ and Me-TTFTB⁴⁻ were calculated in ideal positions with isotropic displacement parameters. The coordinated benzoate anion, free solvent molecules of DMF or cyclohexane for compounds 2, I₃⁻@2, Ag NPs@2, and Au NPs@2 were highly disordered and were not successfully located or refined. The diffuse electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.^{$\frac{3}{2}$} The contents of the solvent region are not represented in the unit cell contents in crystal data. Attempts to precisely refine the solvent molecules were unsuccessful due to the disorder of solvent molecules and the adjacent heavy Zr atoms. Therefore, the content of solvent molecules was calculated from TGA (the weight loss before 120 °C is attributed to the removal of H₂O in the pore, and the weight loss between 120 to 220 °C is assigned to the DMF). The proposed formula, [Zr₆(Me-TTFTB)_{1.5}O₄(OH)₄(C₆H₅COO)₆]•20(H₂O)•4(C₃H₇ON), was further confirmed by elemental analysis (Calcd: C,42.14; H, 4.40; N, 1.77%. Found: C, 40.06; H, 4.10; N, 1.98%). The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1850018, 1974366, 1850014, 1850017, 1850015, and 1850016 for TTFTB-OEt and compounds 1, 2, I₃⁻@2, Ag NPs@2, and Au NPs@2, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. All relevant data supporting the findings of this study are available from the corresponding authors on request.

	1
Empirical formula	$C_{34}H_{16}Zr_3O_{16}S_4$
Formula weight	1082.41
Temperature (K)	298(2)
Crystal system	orthorhombic
Wavelength (Å)	1.54184
Space group	<i>Cmmm</i> (No. 65)
a	22.8669
b	40.1130
c	13.2921
Volume (Å ³)	12192.3
Z	4
2θ range (°)	2.35-40
R_p	3.69%
R_{wp}	4.15%

 Table S1 Crystal data and structure refinement parameters for compound 1.

	2	I ₃ ⁻ @ 2
Empirical formula	$C_{63}H_{40}O_{32}S_6Zr_6$	$C_{42}H_{26.67}O_{21.33}S_4Zr_4I_3$
Formula weight	2048.63	1746.45
Temperature (K)	100	100
Crystal system	Cubic	Cubic
Wavelength (Å)	0.71073	0.71073
Space group	<i>Pm-3m</i> (No. 221)	<i>Pm-3m</i> (No. 221)
Unit cell dimensions (Å,°)		
a, b, c	36.1380(13)	36.1397(4)
α, β, γ	90	90
Volume (Å ³)	47195(3)	47201.3(16)
Z	8	12
Calculated density (gcm ⁻³)	0.577	0.737
F(000)	8080	9988
Absorption coefficient, μ/mm^{-1}	0.336	1.587
No. of reflections measured	89363	282054
No. of independent reflections	7581	8136
θ (°)	1.0-24.7	0.7-22.0
R _{int}	0.072	0.014
$R_{I}, wR_{2}[I \geq 2\sigma(I)]$	0.0760/ 0.2258	0.0330/ 0.1159
R_1 , wR_2 [all data]	0.0840/ 0.2322	0.0372/ 0.1169
GOF	1.14	0.93
Largest diff. peak and hole($e^{A^{-3}}$)	0.71 /-1.23	0.46 / -1.62

Table S2 Crystal data and structure refinement parameters for compounds 2 and $I_3^-@2$.

 $\overline{{}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}}.$

	TTFTB-OEt
Empirical formula	$C_{42}H_{36}O_8S_4\\$
Formula weight	796.95
Temperature (K)	153
Crystal system	Triclinic
Wavelength (Å)	0.71073
Space group	<i>P</i> -1 (No. 2)
a	5.649(3)
b	13.944(6))
c	14.154(6)
α	60.717(7)
β	80.065(9)
γ	86.943(10)
Volume (Å ³)	957.2(8)
Z	1
Calculated density (gcm ⁻³)	1.383
F(000)	416
Absorption coefficient, μ/mm^{-1}	0.302
No. of reflections measured	5993
No. of independent reflections	4486
θ (°)	2.9-27.7
R _{int}	0.041
$R_{l}, wR_{2}[I \geq 2\sigma(I)]$	0.0552/ 0.1258
R_1 , wR_2 [all data]	0.0949/ 0.1418
GOF	1.05
Largest diff. peak and hole(eÅ ⁻³)	0.57 / -0.47

 Table S3 Crystal data and structure refinement parameters for compound TTFTB-OEt.

 $\overline{{}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$

C1–C1 ⁱ	1.354 (5)		
S1—C2	1.782 (2)	S2—C1	1.765 (2)
S2—C3	1.767 (3)	C2—C3	1.357 (4)
C1—S1—C2	96.09 (12)	S1—C1—S2	114.39 (15)
C1—S2—C3	95.70 (13)	C1 ⁱ —C1—S1	123.6 (3)
C3—C2—S1	116.1 (2)	C1 ⁱ —C1—S2	122.0 (3)
C2—C3—S2	117.51 (19)		

Table S4 Selected bond lengths (Å) and angles (°) of compound TTFTB-OEt.

Symmetry transformations used to generate equivalent atoms: (i) -x+2, -y+2, -z+1.

	Ag NPs@2	Au NPs@2
Empirical formula	$C_{63}H_{40}O_{32}S_6Zr_6$	$C_{63}H_{40}O_{32}S_6Zr_6$
Formula weight	2048.63	2048.63
Temperature (K)	100	100
Crystal system	Cubic	Cubic
Wavelength (Å)	0.71073	0.71073
Space group	<i>Pm-3m</i> (No. 221)	<i>Pm-3m</i> (No. 221)
a, b, c	35.7905(9)	35.7905(9)
α, β, γ	90	90
Volume (Å ³)	45846(2)	45846(2)
Z	8	8
Calculated density (gcm ⁻³)	0.594	0.594
F(000)	8080	8080
Absorption coefficient, μ/mm^{-1}	0.346	0.346
No. of reflections measured	129625	356116
No. of independent reflections	3400	6880
θ (°)	1.0-18.6	0.8-24.1
R _{int}	0.168	0.205
$R_{I}, wR_{2}[I \ge 2\sigma(I)]$	0.1040/ 0.3008	0.1261/ 0.3307
R_1 , wR_2 [all data]	0.1195/ 0.3169	0.1654/ 0.3471
GOF	1.30	1.12
Largest diff. peak and hole($e^{A^{-3}}$)	0.98/-0.50	1.19 /-0.77

Table S5 Crystal data and structure refinement parameters for compounds Ag NPs@2 and AuNPs@2.

 $\overline{{}^{a}R1 = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|, wR_{2}} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$

		2		
C10—C10 ^{vii}	1.23 (2)	C10'—C10' ^{vii}	1.33 (4)	
S1—C10	1.767 (7)	S1—C9	1.783 (6)	
S1'—C10'	1.758 (9)	S1'—C9	1.783 (7)	
	I	₃ ⁻ @2		
C10—C10 ⁱⁱ	1.401 (8)			
C10—S1	1.723 (2)	C9—S1	1.735 (3)	
Ag NPs@2				
C10—C10 ^{vii}	1.425 (10)	C10'—C10' ^{vii}	1.429 (11)	
S1—C10	1.661 (5)	S1—C9	1.687 (8)	
S1'—C10'	1.659 (8)	S1'—C9	1.696 (9)	
Au NPs@2				
C10-C10 ^{vii}	1.38 (3)	C10'—C10' ^{vii}	1.37 (4)	
S1—C9	1.677 (8)	S1—C10	1.701 (8)	
S1'—C10'	1.681 (9)	S1'—C9	1.700 (8)	

Table S6 The central C-C and C-S bond length in 2, $I_3^-@2$, Ag NPs@2 and Au NPs@2.

(vii) -*x*, -*y*+1, *z*; (ii) -*x*, -*y*+1, *z*.



Figure S1. (a) The configuration between the TTF motif and benzene rings in the compound TTFTB-OEt. Plane 1 contains S1, S2, S1, and S2; Plane 2 contains C6, C8, C9, and C5; Plane 3 contains C14, C15, C17, and C18. (b) The configuration between the TTF motif and benzene rings in the compound Me-TTFTB in compound **2**. Plane 1 contain C9, C9, C9, and C9; Plane 2 contain C3, C4, C6, and C7.



Figure S2. Ab initio powder X-ray diffraction crystal structure determination and Rietveld refinement of compound 1.



Figure S3. The three-dimensional framework compound 1 viewed in the *a* and *b* direction.



Figure S4. The three-dimensional framework compound **1** viewed in the [**110**] and *c* direction (the green dotted line highlights a pore diameter of 13.7 Å).



Figure S5. The asymmetric unit of compound **2**. One disordered phenyl ring of benzoate anion was omitted. Displacement ellipsoids are drawn at the 50% probability level.



Figure S6. The coordination environment of Me-TTFTB^{4–} and Zr^{4+} ions in compound **2**. The H atoms connected to carbons are omitted for clarity.



Figure S7. ¹H-NMR spectra of PhCOOH (insert picture) and D_2SO_4 dissolved compound 2 in d_6 -DMSO.



Figure S8. The Topologically analysis for compounds 1 and 2. (a) 8-connected and (b) 6-connected Zr_6 clusters. Two linked 3-connected TTFTB (c) and Me-TTFTB (d) nodes. Topology result for compounds 1 (e) and 2 (f).



Figure S9. Three types of cages in compound 2.

Stability and Porosity Tests

Samples for the stability test are prepared with the following procedure: 10 mg of samples 1 or 2 were added in the 1 mL of solvents or solutions with different pHs (HCl and NaOH solutions) for 24 hours without stirring. During this period, there is no pH and color change of the solution (the solution will be red when samples are added in the solution of pH 13 and 14.) were observed.



Figure S10. X-ray powder diffraction patterns of compound 2 in different organic solvents or in air for 24 hours.



Figure S11. X-ray powder diffraction patterns of compound **2** in different pH aqueous solutions for 24 hours.



Figure S12. The N_2 adsorption-desorption isotherms of compound **2** after soaking in the pH=1 and pH=12 solution at 77 K. These results show that compound **2** keep most of the framework in the pH=1 and pH=12 solution.



Figure S13. X-ray powder diffraction patterns of compound 1 in different organic solvents or in air for 24 hours.



Figure S14. X-ray powder diffraction patterns of compound **1** in different pH aqueous solutions for 24 hours.



Figure S15. The TGA plots of compounds 1 and 2 in N_2 atmosphere.

Probing Redox Activity of Compounds 1 and 2



Figure S16. Cyclic voltammograms of Me-H₄TTFTB performed over three consecutive cycles (a) and different scan rates (b). The experiments were conducted in 0.1 M LiBF_4 in DMF electrolyte.



Figure S17. Solid state cyclic voltammogram of compound **1** swept anodically at scan rates of 25-250 mV/s where the arrow indicates the direction of the forward scan.



Figure S18. Solid state CV of compound **1** upon cycling anodically at 100 mV/s three times where the arrow indicates the direction of the forward scan.



Figure S19. Solid state square wave voltammogram of compound **1** at an amplitude of 25 mV and a frequency of 15 Hz against the CV at 100 mV/s where the arrow indicates the direction of the forward scan.



Figure S20. Solid state cyclic voltammogram of compound **2** swept anodically at scan rates of 25-250 mV/s where the arrow indicates the direction of the forward scan.



Figure S21. Solid state CV of compound **2** upon cycling anodically at 100 mV/s three times where the arrow indicates the direction of the forward scan.



Figure S22. Solid state square wave voltammogram of compound **2** at an amplitude of 25 mV and a frequency of 15 Hz against the CV at 100 mV/s where the arrow indicates the direction of the forward scan.



Figure S23. Photographs showing the visual color change before and after crystals of 2 were soaked in a cyclohexane solution of I_2 , scale bar: 100 μ m.



Figure S24. The asymmetric unit of $I_3^-@2$. Displacement ellipsoids are drawn at the 50% probability level. The asymmetric unit contains one Zr^{4+} ion, a quarter of Me-TTFTB⁴⁻ ligand, a quarter of I_3^- ion, two thirds of O^{2-} ion, two thirds of OH^- ion and one benzoic acid anion (Owing to the disorder of phenyl ring, only the COO⁻ was shown in the figure).

Exp for Au NPs@2 Exp for Pd NPs@2 Exp for Ag NPs@2 Exp for Ag NPs@2 Exp for Is @2

20

15

In-situ Generation of Metal Nanoparticles

10

Figure S25. X-ray powder diffraction patterns of compounds $I_3^-@2$, Ag NPs@2, Pd NPs@2, and Au NPs@2. The diffraction peaks of (100) families are stronger than expected due to the preferred orientation of cubic crystals.

25

2-Theta (°)

30

35

40

45

50



Figure S26. The IR spectra for 1, 2, I_3 ^{-@1} and I_3 ^{-@2}.



Figure S27. The TGA plot of $I_3^-@1$ and $I_3^-@2$ in N₂ atmosphere.



Figure S28. X-ray photoelectron spectra for compounds 2 and $I_3^-@2$.



Figure S29. The solid state EPR spectra of $I_3^-@2$ at 110 K. Insert shows the spectrum of compounds 2, which is EPR silent.



Figure S30. The solid state EPR spectra of compounds $1, I_3^-@1$, Ag NPs@1, Pd NPs@1, and Au NPs@1 at 110 K.



Figure S31. Photographs showing the visual color change of Me-H₄-TTFTB solution were mixed with a methanol solution of AgNO₃, PdCl₂, and KAuCl₄, respectively.



Figure S32. Photographs showing the visual color change of Ag NPs, Pd NPs, and Au NPs after crystals of **2** were soaked in a methanol solution of AgNO₃, PdCl₂, and KAuCl₄, respectively, scale bar: $100 \,\mu$ m.



Figure S33. The average size of Ag NPs@2, Pd NPs@2, and Au NPs@2 are 1.83 ± 0.30 , 1.94 ± 0.34 , and 1.93 ± 0.37 nm in diameter, respectively.



Figure S34. Energy dispersive spectroscopic data for compound **2** after it was immersed in 0.1 M MeOH solution of AgNO₃.



Figure S35. Energy dispersive spectroscopic data for compound **2** after it was immersed in 0.1 M MeOH solution of PdCl₂.



Figure S36. Energy dispersive spectroscopic data for compound **2** after it was immersed in 0.1 M MeOH solution of KAuCl₄.



Figure S37. Electron density map for Au NPs@2 single crystal structure showing strong residual electron density in the small cavities.



Figure S38. The TGA plots of desolvation Ag NPs@2, Pd NPs@2 and Au NPs@2 in Air atmosphere. Compared to compound 2, the difference in weight loss is +3.94%, +3.60%, +5.58% for Ag NPs@2, Pd NPs@2 and Au NPs@2, respectively. These values are corresponded to the added residue of Ag₂O (3.70 %), PdO (3.90%) and Au₂O₃ (4.38%).



Figure S39. X-ray photoelectron spectra for compounds 2, Ag NPs@2, Pd NPs@2, and Au NPs@2.



Figure S40. X-ray photoelectron spectra of Ag NPs@2.



Figure S41. X-ray photoelectron spectra of Pd NPs@2.



Figure S42. X-ray photoelectron spectra of Au NPs@2.



Figure S43. The solid state EPR spectra of compounds 2 and Ag NPs@2 at 110 K.



Figure S44. The solid state EPR spectra of compounds 2 and Pd NPs@2 at 110 K.



Figure S45. The solid state EPR spectra of compounds 2 and Au NPs@2 at 110 K.



Figure S46. The IR spectra for Ag NPs@1 and Ag NPs@2. The shoulder peak around 1383 cm⁻¹ can be attributed to the vibration of NO₃⁻.



Figure S47. Photographs showing the visual color change between nanoscale samples of compounds 1, Ag NPs@1, Pd NPs@1, and Au NPs@1.



Figure S48. X-ray powder diffraction patterns of compounds $I_3^-@1$, Ag NPs@1, Pd NPs@1, and Au NPs@1.



Figure S49. The TGA plots of desolvation Ag NPs@1, Pd NPs@1, and Au NPs@1 in Air atmosphere.



Figure S50. X-ray photoelectron spectra for compounds 1, $I_3^-@1$, Ag NPs@1, Pd NPs@1, and Au NPs@1.



Figure S51. X-ray photoelectron spectra for compounds 1 (a) and $I_3^-@1$ (b) (c).



Figure S52. X-ray photoelectron spectra of Ag NPs@1.



Figure S53. X-ray photoelectron spectra of Pd NPs@1.



Figure S54. X-ray photoelectron spectra of Au NPs@1.



Figure S55. SEM images of compounds 1 (a) and $I_3^-@1$ (b).



Figure S56. SEM images of compounds Ag NPs@1 (a), Pd NPs@1 (b), and Au NPs@1 (c).



Figure S57. Energy dispersive spectroscopic data for compound 1.



Figure S58. Energy dispersive spectroscopic data for $I_3^-@1$.



Figure S59. Energy dispersive spectroscopic data for compound **1** after immersion in 0.1 M MeOH solution of AgNO₃.



Figure S60. Energy dispersive spectroscopic data for compound **1** after immersion in 0.1 M MeOH solution of PdCl₂.



Figure S61. Energy dispersive spectroscopic data for compound **1** after immersion in 0.1 M MeOH solution of KAuCl₄.



Figure S62. The TEM image and the average size of Ag NPs in 1.



Figure S63. The TEM image and the average size of Pd NPs in 1.



Figure S64. The TEM image and the average size of Au NPs in 1.



Figure S65. The catalysis reaction of Pd NPs@2.



Figure S66. Leaching test for the oxidation reaction of benzyl alcohol over Pd NPs@ 2 catalyst after 13 hours.



Figure S67. The aldehyde selectivity with or without Pd NPs@ 2 catalyst in 24 hours.



Figure S68. The PXRD patterns of Pd NPs@ 2 catalyst after the recycling test. It should be noted that the first peak at 2.5 degree overlaps with the background, therefore it is not very obviously.

Name	Ag NPs@1	Pd NPs@1	Au NPs@1	Ag NPs@2	Pd NPs@2	Au NPs@2
Formula (Zr:M)	6:1	6:1	9:1	24:3	24:3	12:1
ICP (Zr:M)	6:1.02	6:1.11	9:3.28	24:3.15	24:3.09	12:1.27
EDX (Zr:M)	6:0.84	6:0.82	9:2.27	24:2.68	24:2.38	12:0.86

Table S7 SEM-EDX and ICP-AES data for MNPs@1 and MNPs@2.

Table S8 Oxidation reaction of benzyl alcohol catalyzed by Pd NPs@2 and recycling test.^a

Entry	Cycle	Conv. (%)	Aldehyde yield (%)	Standard deviation (%)
1	-	100	52.3	0.8
2	1	100	51.0	0.4
3	2	100	52.8	1.0
4	3	100	51.6	0.7

^aReaction conditions: Generally, a mixture of benzyl alcohol (0.1 mmol), and catalyst (5 mg) and 2 mL cyclohexane were charged in a 10 mL round-bottom flask and stirred under 0.1 MPa O_2 at 90 °C for 22 h. The products were identified by a GC-MS. Pd NPs@2 was recycled from the reaction mixture by centrifugation and reused in successive runs. Standard deviation obtained by three recycling tests.

Entry	Substrates	Conv. (%)	Aldehyde yield (%)
1	- С- Сон	51.7	100
2	р	79.7	49.7
3	FOH	60.4	42
4	вгОн	5.2	77
5	02N-OH	0.1	100
6	ОН	24.6	86.2
7	С	24.8	100

 Table S9 Oxidation reaction of various substituted benzyl alcohols catalyzed by Pd NPs@2.

^a Reaction conditions: Generally, a mixture of alcohol (0.1 mmol), and catalyst (5 mg) and 2 mL cyclohexane were charged in a 10 mL round-bottom flask and stirred under 0.1 MPa O_2 at 90 °C for 22 h. The products were identified by a GC-MS.

Name	Conv. (%)	Aldehyde yield (%)
Pd/C	100	98.0
Me-H ₄ -TTFTB	1.20	0
2	1.28	100
Pd NPs@2	100	52.3

Table S10 Oxidation reaction of benzyl alcohol catalyzed by Pd/C, Me-H₄-TTFTB or compound 2^{a} .

^a Reaction conditions: Generally, a mixture of benzyl alcohol (0.1 mmol), and catalyst (5 mg) and 2 mL cyclohexane were charged in a 10 mL round-bottom flask and stirred under 0.1 MPa O_2 at 90 °C for 22 h. The products were identified by a GC-MS.

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Author Contributions

J.S. and S.Y. contributed equally. J.Z., H.-C.Z., J.S., and S.Y. conceived and designed the project. J.S., S.Y., T.W. performed the experiments. J.-W.Z. conduct the Rietveld refinement. S. Y., J. S., C.T.L., J.Z., and H.-C.Z., drafted the original manuscript. All authors have discussed the results and given approval to the manuscript.