Electronic Supplementary Information

High loading of Pd nanoparticles enhanced by chelating 1,2-diol subunit in flexible porous polymers for catalytic reduction of 4-nitrophenol

Zhi-Cun Wang, [a] Boya Kuang, [b] Hanyuan Chen, [b] Nicolas Bogliotti, [c] Ran Guo, [d] Yan Liu, [b] Jin-Xiu Zhou[a]* and Mu-Hua Huang[a]*

[a]School of Materials Science and Engineering, Beijing Institute of Technology, No. 5, Zhongguancun South Street, Beijing 100081, China

[b]Experimental Center for Advanced Materials, Beijing Institute of Technology, No. 5, Zhongguancun South Street, Beijing 100081, China

[c]Université Paris-Saclay, ENS Paris-Saclay, CNRS, Photophysique et Photochimie Supramoléculaires et Macromoléculaires, 91190, Gif-sur-Yvette, France

[c]Perkinelmer Management (Shanghai) Co., Ltd. No.1670, Zhangheng Road, Shanghai, 201203, China

Contents

1. General information for materials and measurements

1.1 Chemicals and materials

All chemicals including toluene, chloroform, methanol, ethanol, ethyl acetate, N, N'-dimethyl acetamide (DMAc) were purchased from commercial suppliers (Beijing Tongguang Fine Chemical Co.) and used without further purification, unless otherwise noted. The monomers of 9,9'-Bis(4-hydroxylphenyl)fluorene (BHPF) and 4,4'-difluorobenzoin were purchased from energy-chemical Co., and they were recrystallized from methanol and ethyl acetate correspondingly before use. Anhydrous K_2CO_3 was bought from Tianjin Zancheng Co., which was meshed into powder and dried in oven (100 ºC) overnight before use. Dueterated solvents such as $CDCl_3$ and DMSO-d6 were purchased from Qingdao Tenglong Tech. Co.

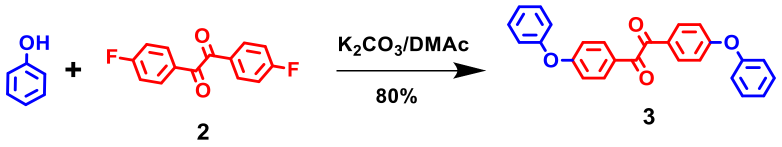
1.2 Characterization and instruments

Solution ^{1}H-NMR spectra were taken by Varian Mercury-400 MHz and Bruker Avance III 400 MHz NMR (^{1}H at 400 MHz, ^{13}C at 100 MHz). Solid-state ^{13}C Cross-Polarization Magic Angle Spinning (CP/MAS) NMR spectra were obtained on a Bruker Avance III 400 MHz Wide Bore spectrometer (14.2 T). A 4.0 mm MAS probe and ZrO_2 motor were used, and spin rates at 13 kHz. Chemical shifts (δ) are reported in ppm. ^{13}C Solid State Nuclear Magnetic Resonance T1 relaxation time T1 measurements were performed on Bruker Avance III 400 MHz Wide Bore spectrometer (14.2 T). A 4.0 mm MAS probe and ZrO2 motor were used, and spin rates at 13 kHz. a SR pulse sequence were used with τ ranging from 0.1 to 100 s. Spectra were recorded with an acquisition time of 50 ms. Data was analyzed and fitted by topspin 3.5. Infrared spectra were recorded on a PerkinElmer Spectrum Two Fourier transform spectrometer. Elemental analysis was measured in the analytical instrumentation center of Beijing University, Beijing China, by using ElementarVario EL CUBE. Thermogravimetric analysis (TGA) was carried out on a Q600 SDT (TA, US) thermogravimetric analyzer, heated from 25 °C to 800 °C at a rate of 10 °C/minute under N_2 atmosphere. Solution UV-vis spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer. The morphologies of polymers were studied using a Hitachi S4800 scanning electron microscope (SEM) and FEIT T ecnai G2 F30 transmission electron microscope (TEM) working at 300 kV. GPC was measured by Agilent Gel Permeation Chromatography instrument using THF as the mobile phase with eluting rate of 1 ml/min, and monodisperse polystyrene standard sample was used to calibrate. N_2 adsorption/desorption studies were carried out at 77 K using the BET V-sorb 4800 (Chinainstru& Quantumtech (Hefei) Co.,Ltd, China) and MicroActive for ASAP 2460 2.02 (Micromeritics Inc., USA). BET surface area and pore volume were obtained by Brunauer-Emmett-Teller (BET) method between the pressure range of 0.05-0.35 P/P_0. Polymer pore size distributions were calculated from the adsorption branches using non-local density functional theory (NLDFT) methods. Metal ions concentrations were determined by ICP- instrument of Agilent 725 model. Powder XRD analysis was carried out in Bruker D8 Advance, with the range in 10-80^o in a scan rate of 5°/min.

Solid State 13C T1 relaxation time measurements were performed on Bruker Avance III 400 MHz Wide Bore spectrometer (14.2 T). A 4.0 mm MAS probe and ZrO2 motor were used, and spin rates at 13 kHz. A cphirt1 pulse sequence was used with τ ranging from 0.1 to 100 s. Spectra were recorded with an acquisition time of 50 ms. Other parameter follows these setupments: rg=103, D1=10s, L20=3, NS=8. Data was analyzed and fitted by topspin 3.5, Fitting function type was invrec, integral for C-O-C range from 161.9ppm to 156.8ppm, integral for hydroxy carbon range from 80.6ppm to 74.4ppm.

2. Syntheses of model compound and polymers

2.1 The synthesis of model compound 3



To a mixture of phenol (8 mmol, 752.90 mg) and anhydrous potassium carbonate (9.22 mmol, 1.27 g) in a 250 ml flask added DMAc (100 ml) portionwise under N_2 atmosphere carefully. Ten resulted mixture was heated at 150 °C over 10 h, then the mixture was cooled down to 130 °C, to which was added a solution of 4,4’-difluorobenzil

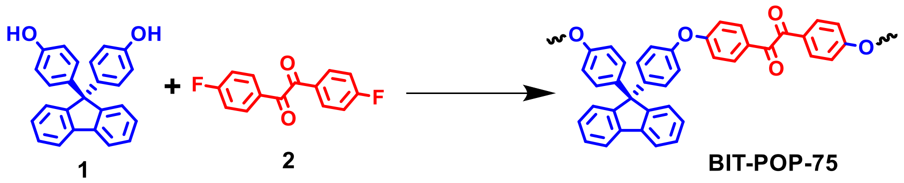
(3.82 mmol, 941 mg) in DMAc (20 ml) through a syringe. And the reaction mixture was heated at 150 °C for further 10 h. When cooling down to room temperature, the reaction mixture was filtered to remove potassium carbonate and the filtrate was poured into 1 M hydrochloric acid. The resulting precipitate was collected and dried at 80 °C in vacuum oven to get the title compound as a brown powder (1.2 g, Yield: 80 %).

^{1}H-NMR (400 MHz, DMSO-d_6) δ(ppm): 7.92 (d, $J = 8.8$ Hz, 4H), 7.48 (t, $J = 8.4$ Hz, 4H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 6H), 7.11 (d, $J = 8.8$ Hz, 4H).

^{13}C-NMR (100 MHz, CDCl$_3$) δ (ppm): 193.2, 163.6, 154.8, 132.4, 130.2, 127.5, 125.1, 120.5, 117.4.

FT-IR (cm^{-1}): 3043(w), 1662(s), 1600(s).

2.2 The synthesis of BIT-POP-75



High Temperature Method: A mixture of 4,4’-difluorobenzil (20 mmol, 4.92 g), 9,9’-bis(4-hydroxyphenyl)fluorene (20 mmol, 7.05 g) and anhydrous potassium carbonate (60 mmol, 8.29 g) in toluene (20 ml) and anhydrous DMAc (40 ml) was heated at 60 °C in a three-necked round bottom flask using a Dean-Stark condenser under an atmosphere of N$_2$. Subsequently, the reaction mixture was heated and stirred vigorously at 165 °C for 40 min. After cooling to room temperature, the viscous reaction mixture was poured into methanol (500 ml) to give a brown suspension with noodles-liked solid, which was stirred for 1 h. The solid product was filtered and collected, and then it was redissolved in CHCl$_3$(100 ml) within 2 h, and then methanol (500 ml) was added to precipitate. The solid product was further collected by filtration, and then washed with water at 100 °C (350 ml) to remove K$_2$CO$_3$. After a pale yellow solid was freeze-dried for 1 day, the titled polymer of BIT-POP-75 was observed (10.0 g, Yield: 86 %).

Low Temperature Method: 4,4’-difluorobenzil (20 mmol, 4.92 g), 9,9’-bis(4-hydroxyphenyl)fluorene (20 mmol, 7.05 g) were added to a dry three-neck round-bottom flask with DMF (100 mL) under an atmosphere of N2. The reaction mixture was stirred at 65 °C until all reagents dissolved. Fine potassium carbonate (60 mmol, 8.29 g) w as gradually added to the system, and then the reaction mixture was stirred for 72 hours. Then, a highly viscous solution was cooled down and poured into water (600 mL). The polymer solid was obtained by filtration. The purification was performed by dissolving the material in chloroform (160 mL) and precipitating from methanol (500 mL). The solid product was further collected by filtration, and then washed with water. The pale yellow solid was freeze-dried for 1 day to get target product (8.6 g, Yield:74.3%).

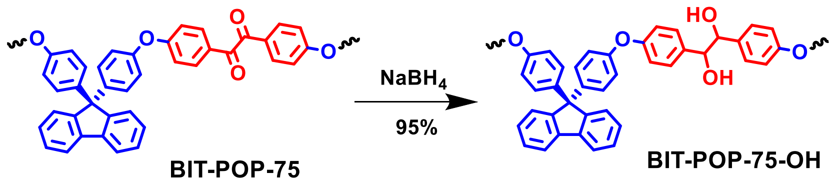
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88(d, *J*=8.4 Hz, 2H), 7.78(d, *J*=7.2 Hz, 2H), 7.41, 7.40, 7.36, 7.30(d, *J*=7.2 Hz, 2H), 7.27, 7.26, 7.22(d, *J*=8 Hz, 2H), 6.97(d, *J*=8.4 Hz, 2H), 6.91(d, *J*=8.4 Hz, 2H).

^{13}C CPMAS δ (ppm): 194.47, 164.50, 153.07, 140.08, 128.53, 65.13.

FT-IR (cm^{-1}): 3041(w), 1672(m), 1589(s)

EA: C, 81.35%; H, 3.86%; O, 11.65%.

2.3 The synthesis of BIT-POP-75-OH



To the solution of BIT-POP-75 (200 mg) in THF (20 ml) was added $NaBH_4$ (400 mg), the resulting pale yellow reaction mixture was stirred vigorously for 24 h. Then the white reaction mixture was quenched with methanol, the solvents were removed under vacuum using rotary evaporation, the white residue was washed with hot water, filtered, and then freeze-dried to afford the title polymer of BIT-POP-75-OH. (191 mg, Yield: 95%).

^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm): 7.88, 7.47, 7.35, 7.27, 7.20, 7.08, 6.84, 5.17.

^{13}C CPMAS δ (ppm): 158.40, 153.97, 140.81, 128.29, 77.42, 65.14.

FT-IR (cm^{-1}): 3558(w), 3031(w), 1600(m).

EA: C, 81.07%; H, 4.67%; O, 11.43%.

3. Preparation of Pd@BIT-POP-75-OH and its catalytic performance

3.1 Loading of Pd NPs on BIT-POP-75-OH to make the catalyst Pd@BIT-POP-75-OH

To a solution of BIT-POP-75-OH (200 mg) in THF (20 ml) was added $Pd(OAc)_2$ (0.4 mmol, 68 mg), the resulted reaction mixture was heated and stirred vigorously at 60 °C for 3 h. After cooling to the room temperature, the reaction mixture was treated with a solution of sodium borohydride (1.5 g) in methanol (20 ml), and the mixture was stirred continuously for 3 h. After that, the solvent was removed under vacuum by rotary evaporation. The titled catalyst of Pd@BIT-POP-75-OH was obtained as a black solid, after the black residue was washed with water for 3 h and freeze-dried for 1 day (245 mg, Yield: 95%, Pd content: 12.53 wt%, quantified by the ICP-OES).

^{13}C CPMAS δ (ppm): 158.68, 153.43, 140.54, 128.25, 79.31, 65.16.

FT-IR (cm^{-1}): 3035(w), 1597(w), 1500(s).

3.2 Catalytic reduction reaction on 4-nitrophenol using Pd@BIT-POP-75-OH

To a 4-NP aqueous solution (3 ml, 0.01 M) in a 20 ml vial was added $NaBH_4$ aqueous solution (9 ml, 0.5 M) and the Pd@BIT-POP-75-OH aqueous dispersion (1 ml, 2.5 mg/ml) in that order, the resulting reaction mixture was stirred vigorously. Over a certain period of time, the reaction mixture was allowed to stand for several seconds. Then 0.5 ml of the mixture solution was taken, the solid was filtered, and the filtrate was diluted to 10 ml of water for UV−vis measurements. The UV absorption spectra of the solution at different times were recorded. To further verify the stability and recyclability of the Pd@BIT-POP-75-OH catalyst, ten turns were cycled under the same conditions as above, and the conversion rate of each time was calculated. The filtered catalyst was used directly for the next run.

4. Figures in ESI

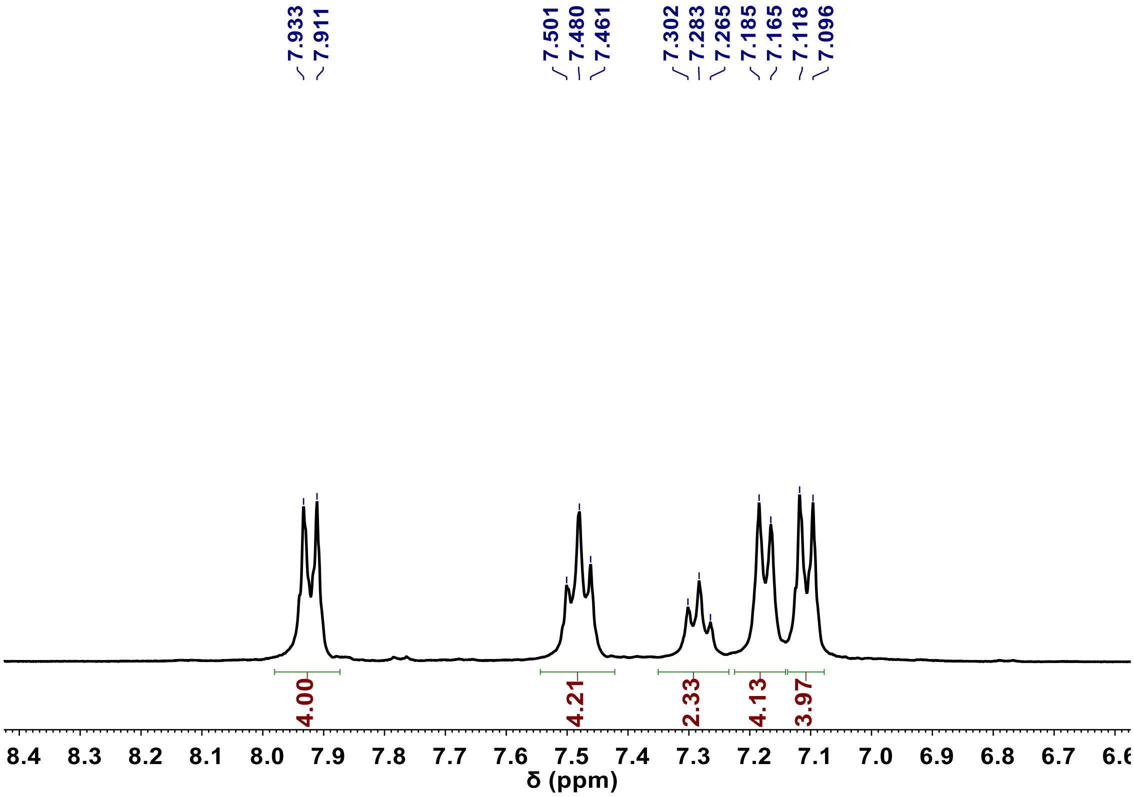


Figure S1 ^{1}H-NMR of model compound (3) in DMSO-*d6*

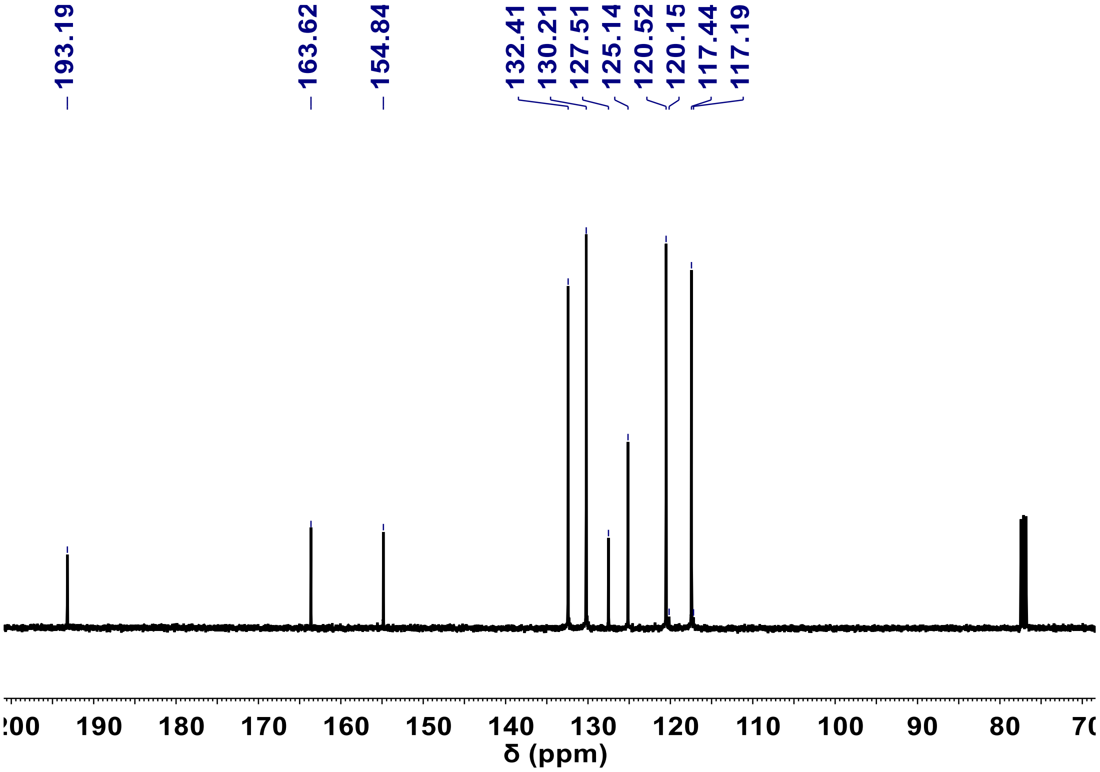


Figure S2 ^{13}C-NMR of model compound (3) in CDCl$_3$

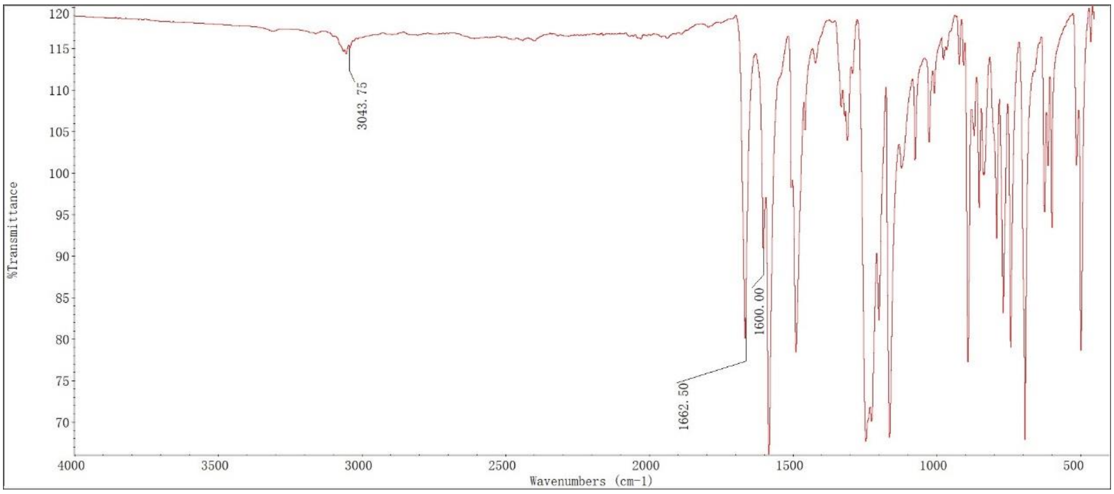


Figure S3 FT-IR of model compound (3)

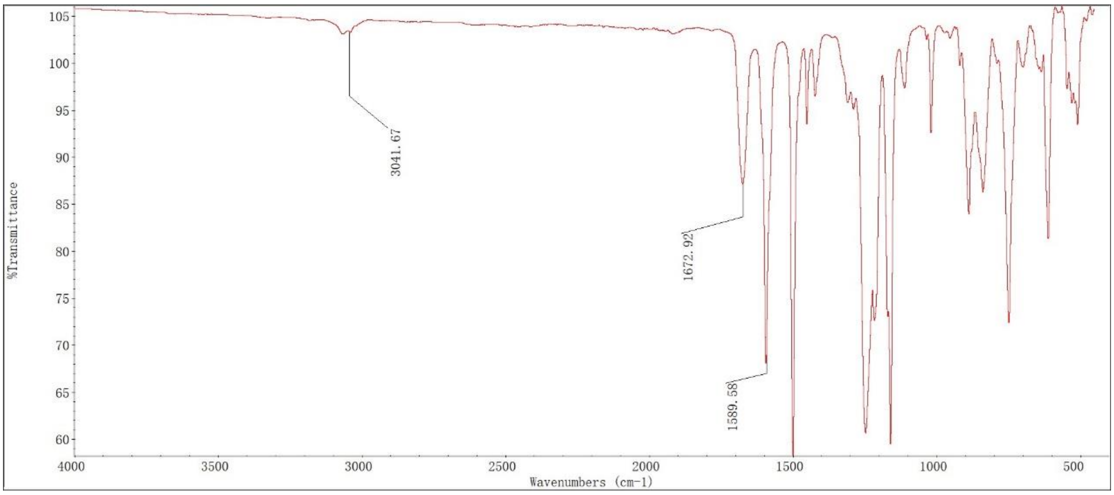


Figure S4 FT-IR of BIT-POP-75

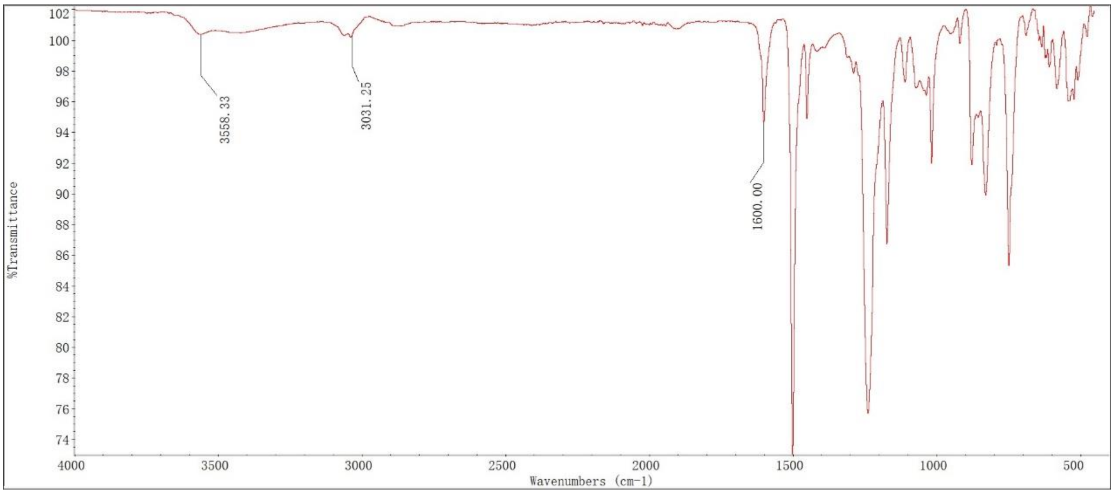


Figure S5 FT-IR of BIT-POP-75-OH

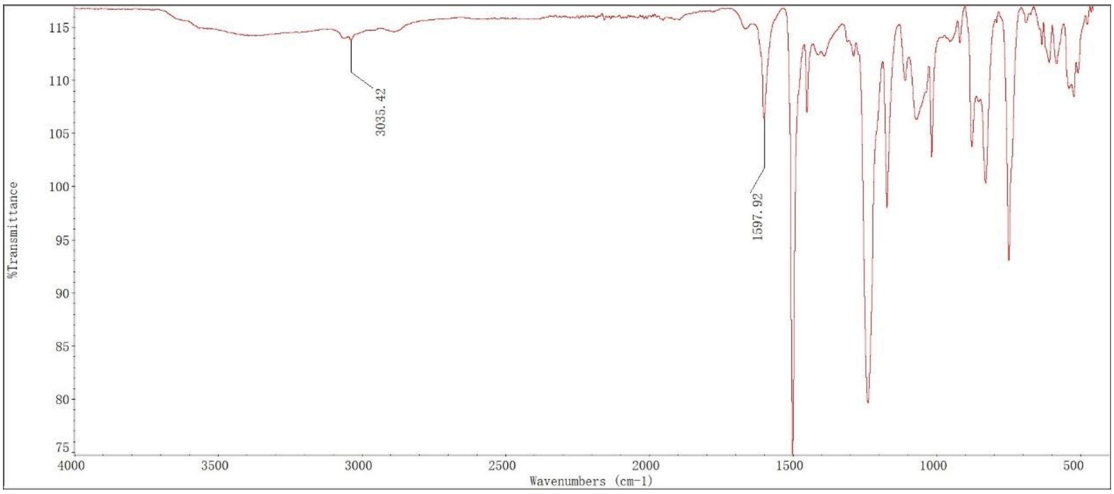


Figure S6 FT-IR of Pd@BIT-POP-75-OH

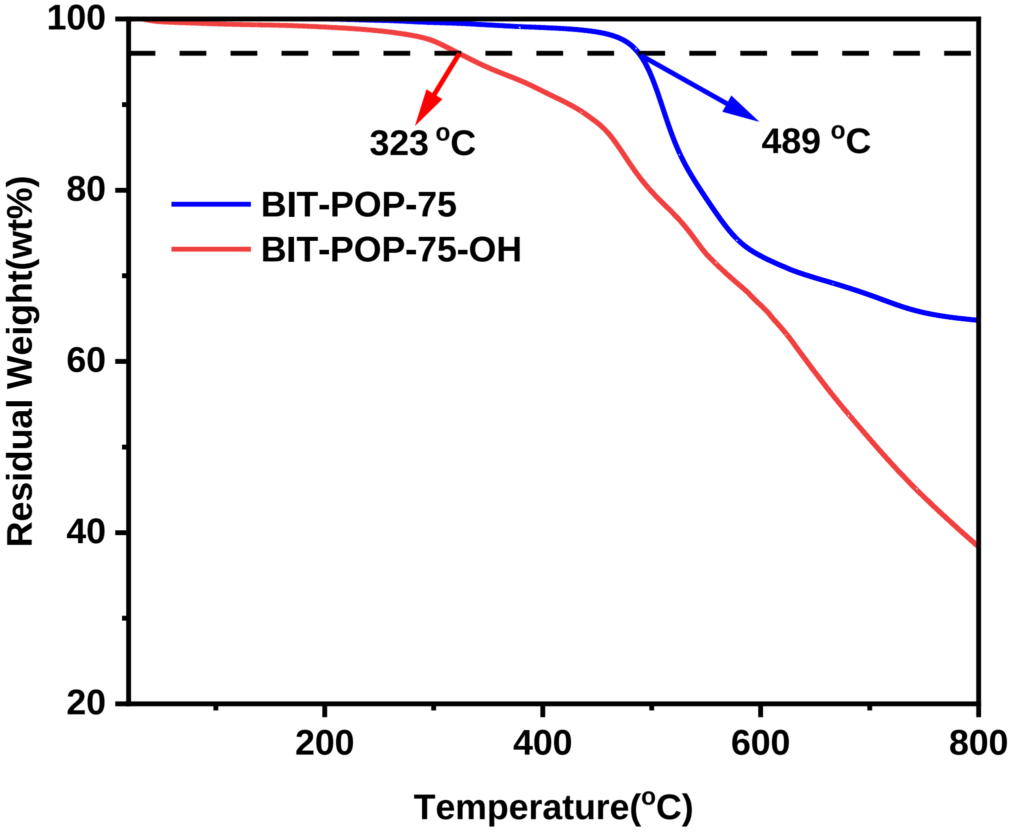


Figure S7 TG of BIT-POP-75 and BIT-POP-75-OH

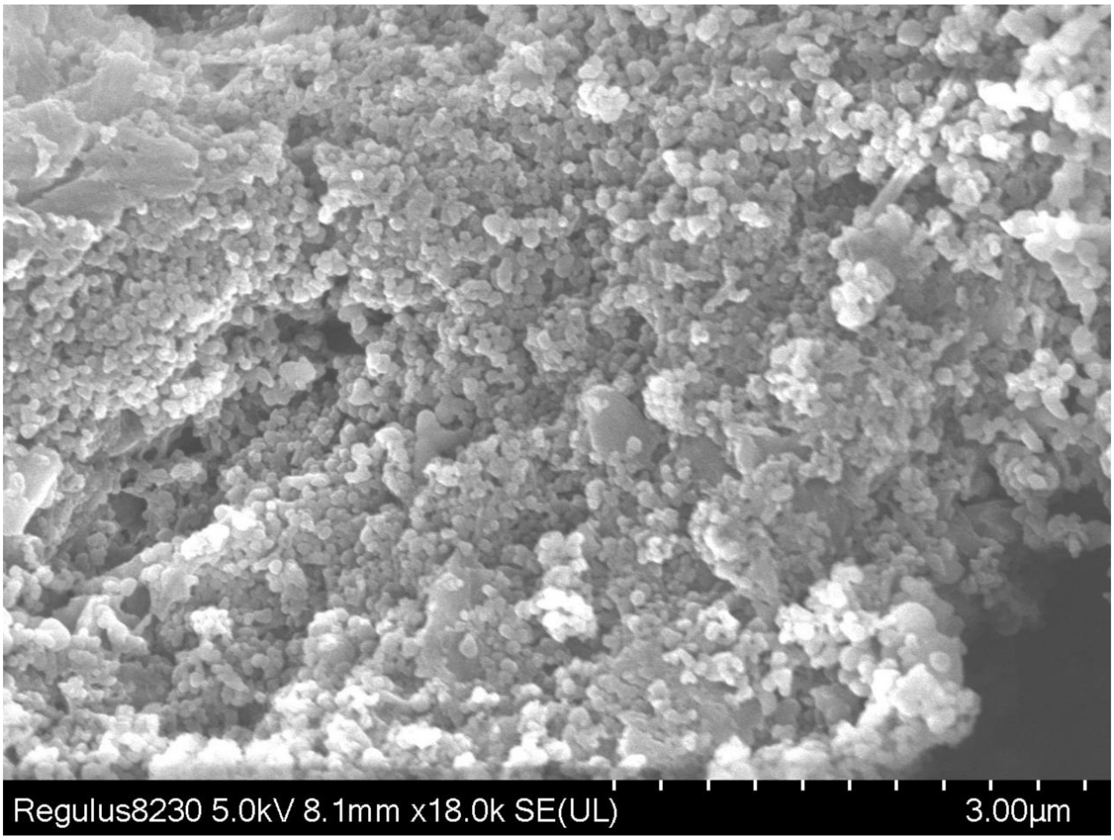


Figure S8 SEM image of BIT-POP-75

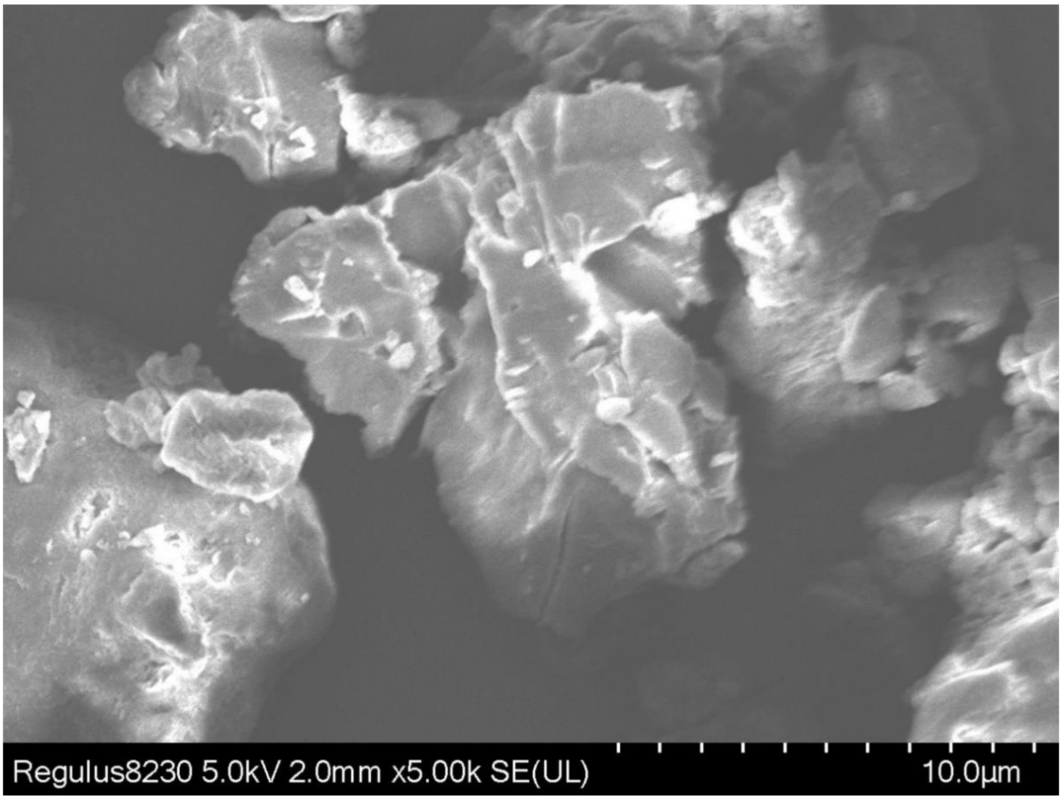


Figure S9 SEM image of BIT-POP-75-OH

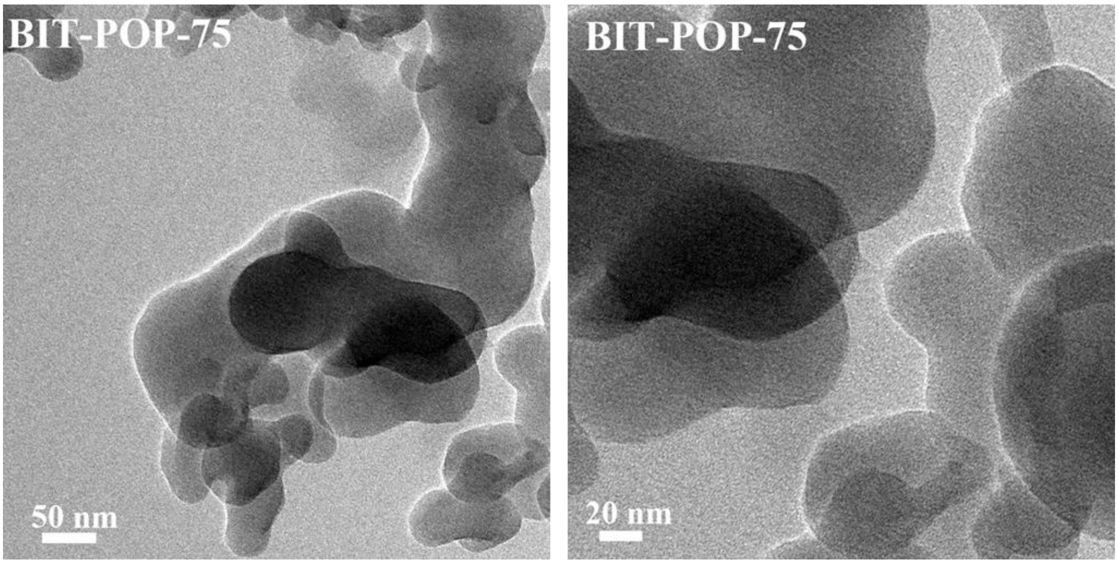


Figure S10 TEM image of BIT-POP-75

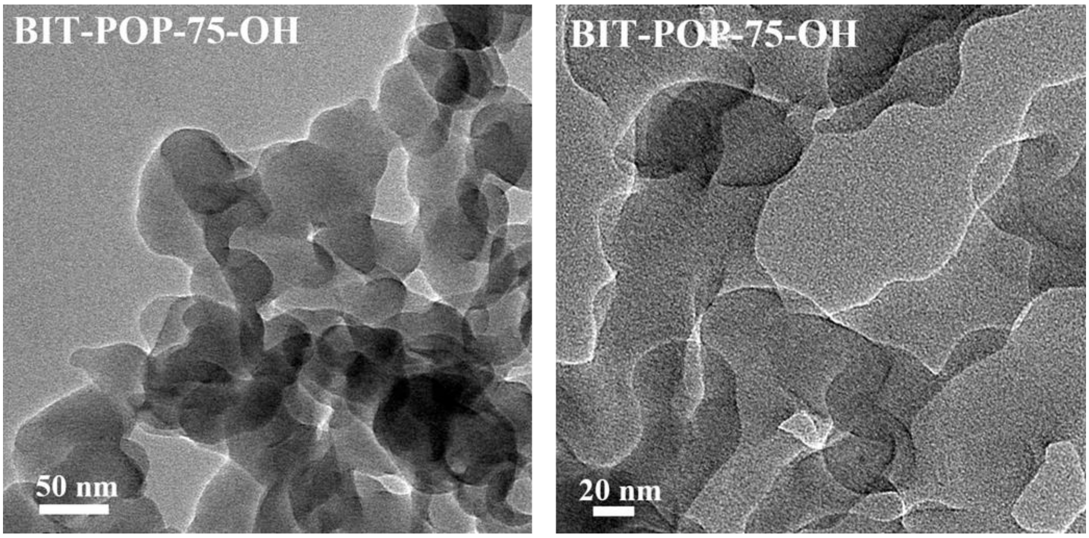


Figure S11 TEM image of BIT-POP-75-OH

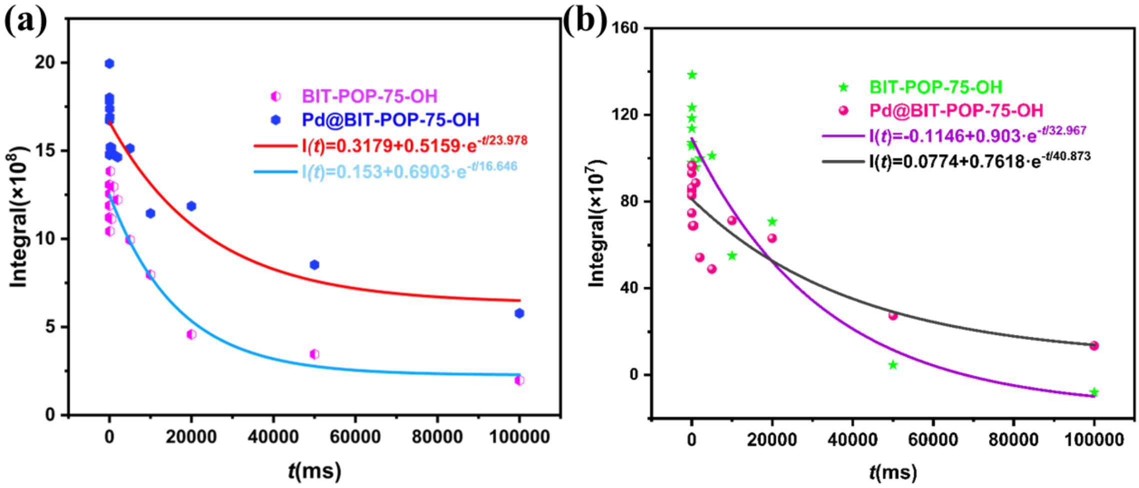


Figure 12. T1 time based on solid-state ^{13}C NMR spectra: (a) Based on Carbon c (158 ppm) and (b) Carbon a (67 ppm) in BIT-POP-75-OH and Pd@BIT-POP-75-OH

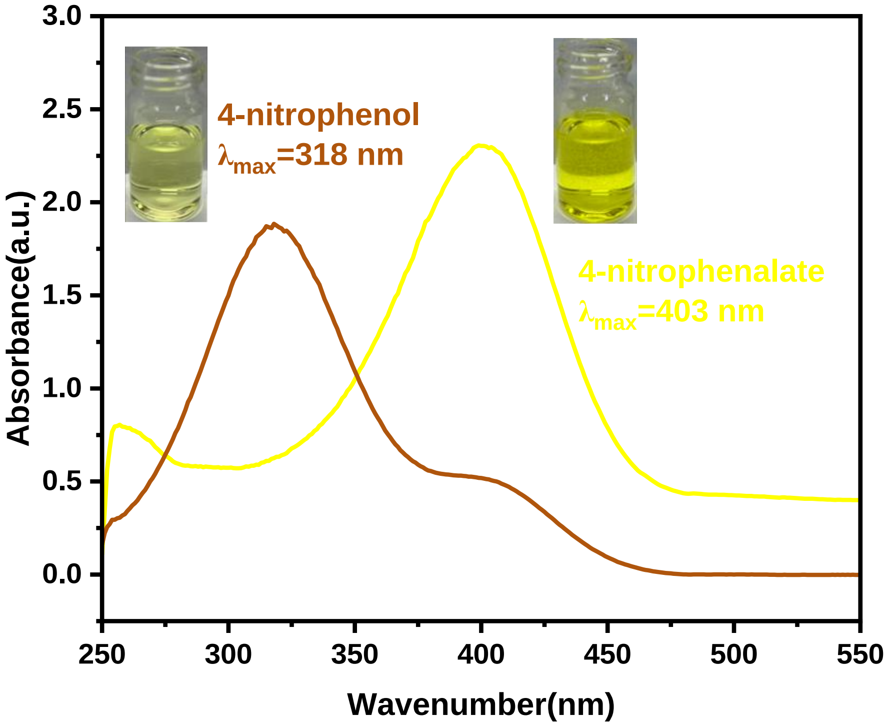


Figure S13 UV-Vis absorption spectra of 4-NP before and after addition of $NaBH_4$ solution

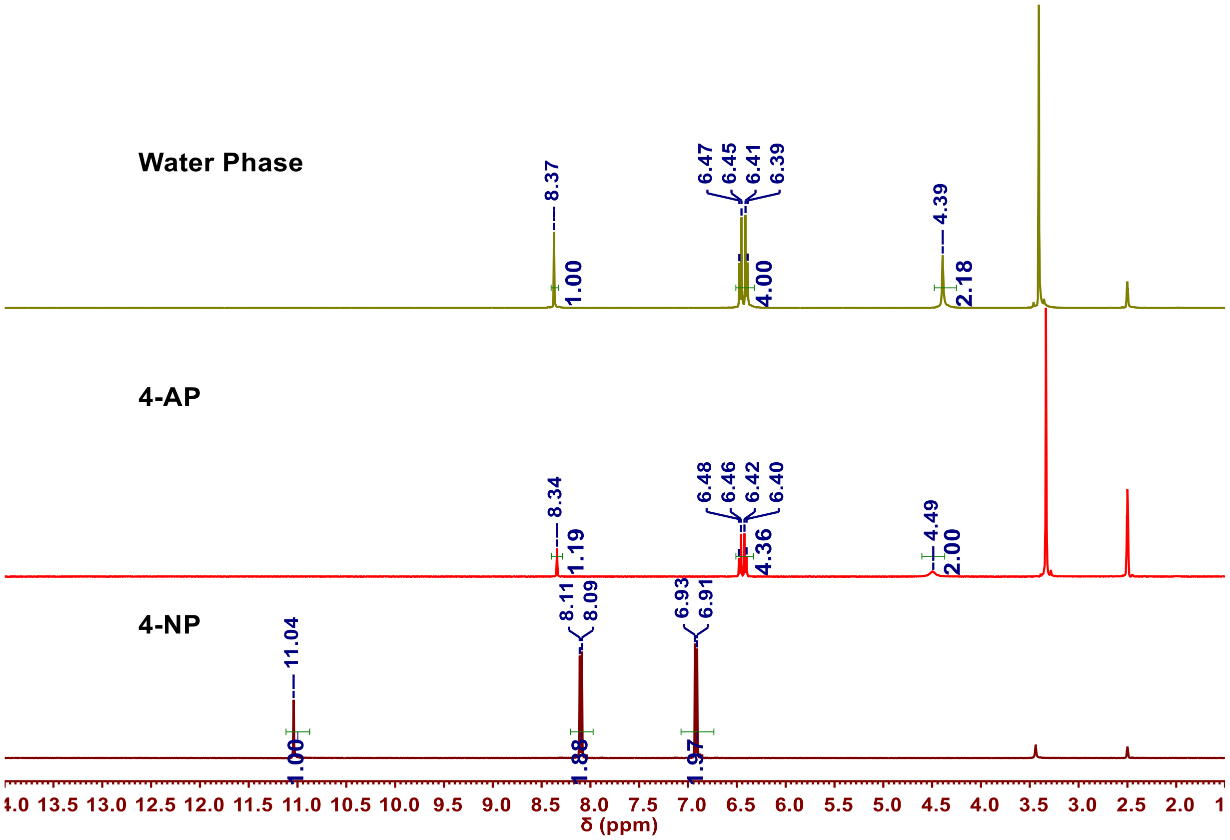


Figure S14 ^1H NMR of 4-NP, 4-AP standard sample and crude product in water phase after catalytic reduction in DMSO-*d6*

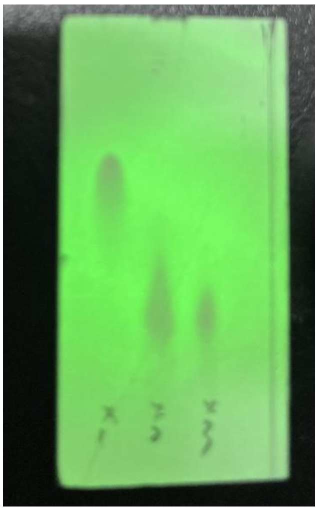


Figure S15 TLC of 1-3(1 means 4-NP, 2 means 4-AP, 3 means crude product after reduction, PE:EA=2:1)

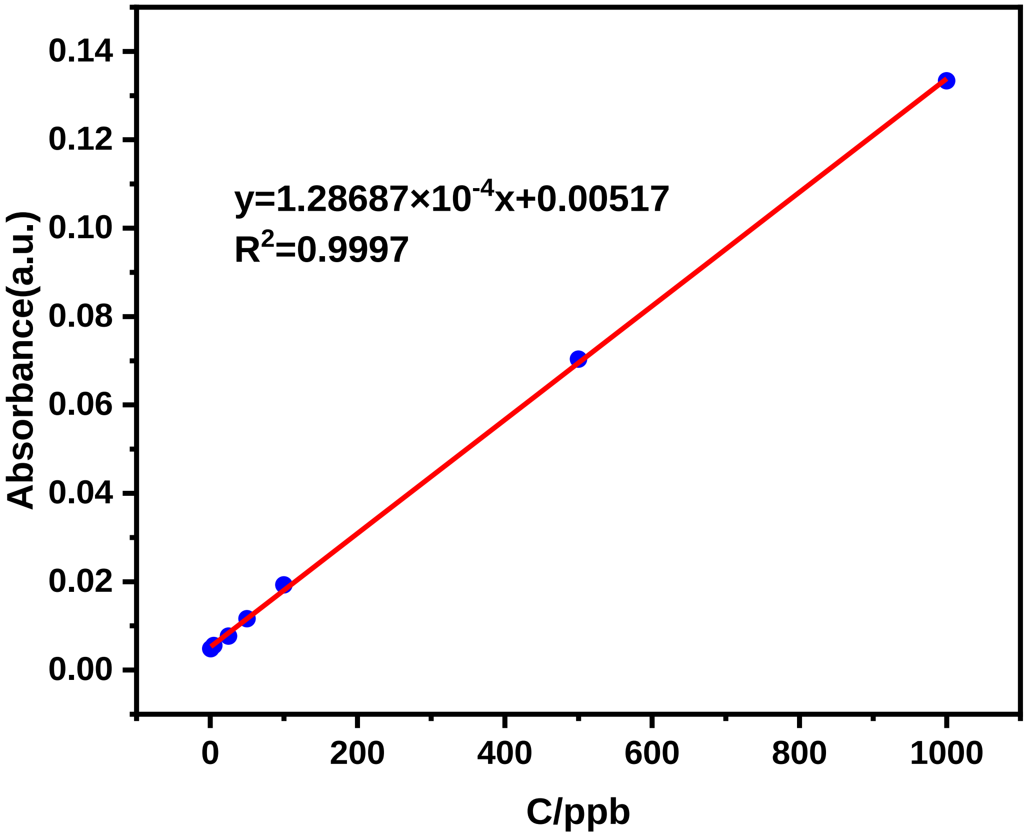


Figure S16 Standard curve of 4-NP in different concentration

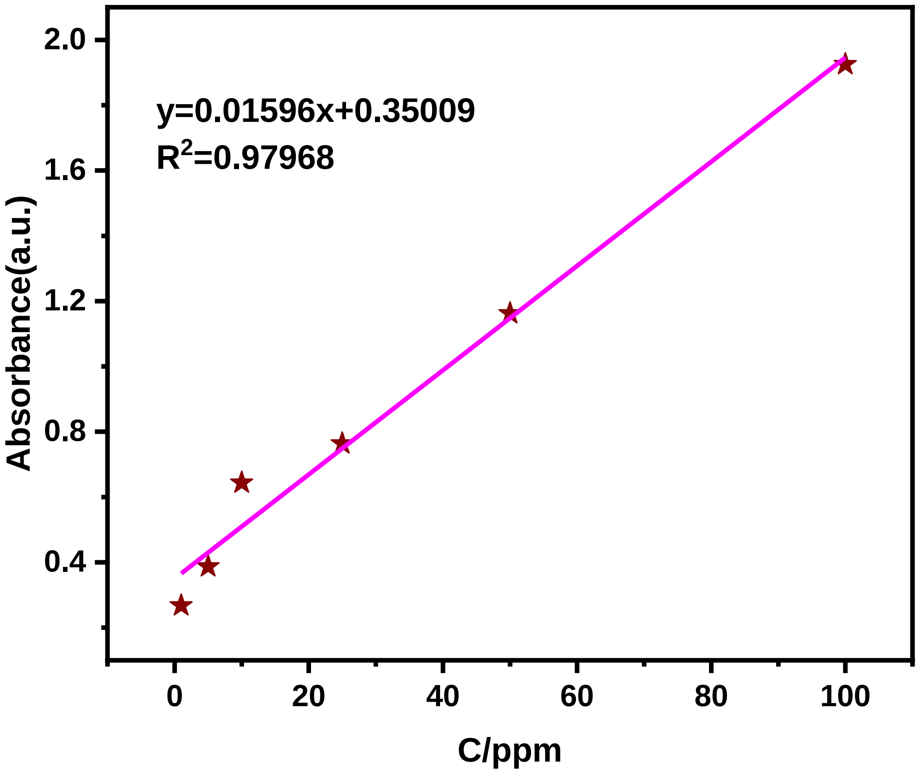


Figure S17 Standard curve of 4-AP in different concentration

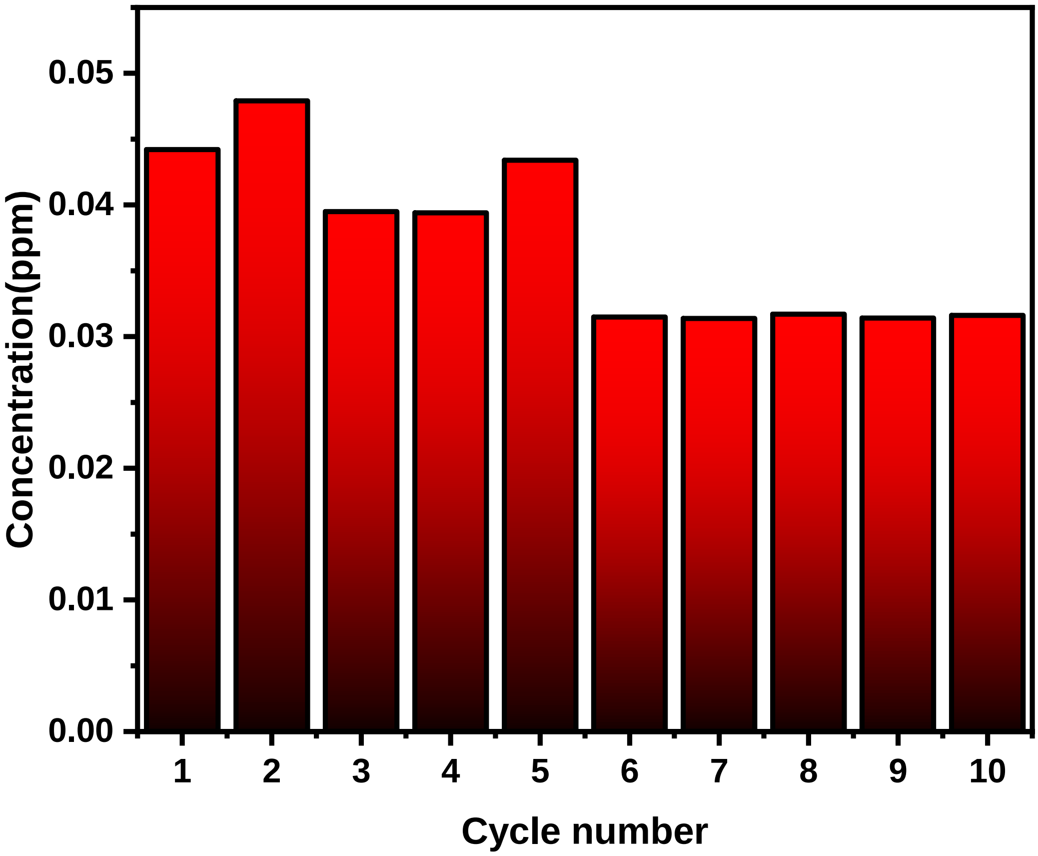


Figure S18 Concentration of palladium in the solution after each cycle of catalyzation

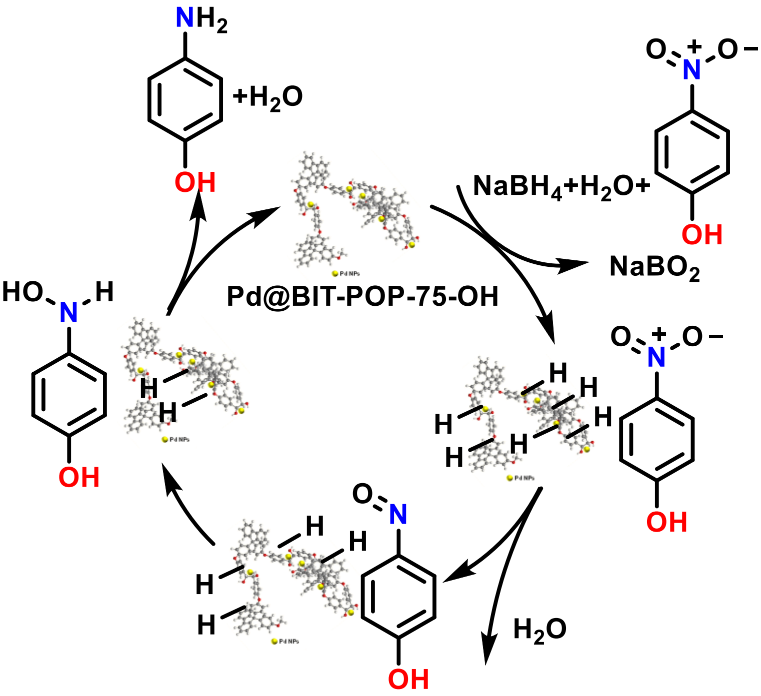


Figure S19. Catalytic mechanism of 4-NP reduced by Pd@BIT-PO-75-OH

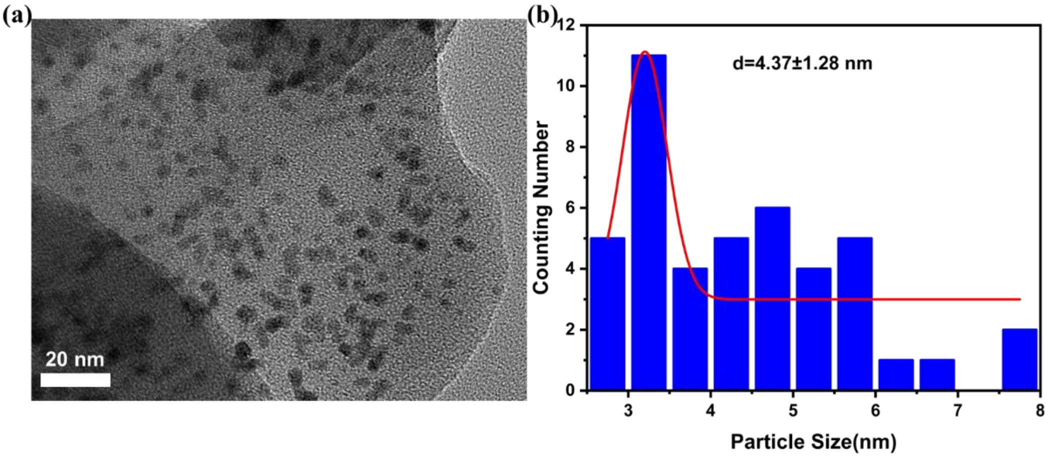


Figure S20 TEM image of recycled Pd@BIT-POP-75-OH after six times (a) and the their diameter distribution of Pd nanoparticles

5. Tables in ESI

Table S1 The BET results of BIT-POP-75-79

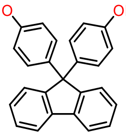
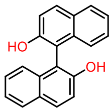
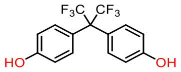
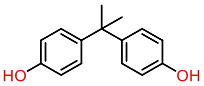
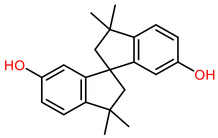
Sample name	Structure of 1,2-diol monomer	BET(m^2/g)
BIT-POP-75		118
BIT-POP-76		7
BIT-POP-77		48
BIT-POP-78		17
BIT-POP-79		22

Table S2 Optimization of polymerization to give BIT-POP-75

Sample Name	GPC results			BET (m^2/g)
	M_n	M_w	PDI	
BIT-POP-75-H[a]	15900	27700	1.74	118
BIT-POP-75-L[b]	6536	8578	1.31	38

[a] The sample obtained by high-temperature method. [b] The sample obtained by low-temperature method.

Table S3 Solubility of BIT-POP-75 and BIT-POP-75-OH

Solvent	BIT-POP-75	BIT-POP-75-OH
DCM	✓	Swell
$CHCl_3$	✓	Swell
1,4-dioxane	✓	✓
THF	✓	✓
DMF	✓	✓
DMAc	✓	✓
NMP	✓	✓
DMSO	✗	✓
CH_3CN	✗	✗
H_2O	✗	✗
MeOH	✗	✗

Table S4 Low field test results of BIT-POP-75 and BIT-POP-75-OH

Samples	T_{21}/ms	T_{22}/ms	A_1/a.u.	A_2/a.u.	Rigid proportions	Flexible proportions
BIT-POP-75	0.0278	0.3588	1	0.0187	98.2%	1.8%
BIT-POP-75-OH	0.026	0.2134	1	0.0289	97.2%	2.8%

Table S5 Elemental analysis of BIT-POP-75 and BIT-POP-75-OH

Samples	Quality Percentage (%)					
	Found values			Theoretical values[a]		
	C	H	O	C	H	O
BIT-POP-75	81.35	3.86	11.65	84.16	4.35	11.50
BIT-POP-75-OH	81.07	4.67	11.43	83.55	5.03	11.41

[a] Theoretical values were calculated assuming an ideal structure of BIT-POP-75 and BIT-POP-75-OH for the elemental analysis.

Table S6 Porosity Parameters of BIT-POP-75, BIT-POP-75-OH and Pd@BIT-POP-75-OH

Samples	$S_{BET}(m^2/g)$	$S_{Lang}(m^2/g)$	Mean diameter of pore(nm)	$V_{micro}(cm^3/g)$[a]	$V_{total}(cm^3/g)$[b]
BIT-POP-75	118	586	21.66	0.008319	0.64
BIT-POP-75-OH	63	373	28.12	0.004676	0.44
Pd@BIT-POP-75-OH	29	165	20.74	0.001172	0.15

[a] Micropore volume calculated from nitrogen adsorption isotherm using the t-plot method. [b] Total pore volume at $P/P_0 = 0.99$.

Table S7 Optimization of catalytic performance

Entry	Catalyst with different Pd content (1 mL, 2.5 mg/mL)	Molar concentration of $NaBH_4$ (9 mL)	The time to fully react
1	BIT-POP-75-OH-12.43wt%	0.1M	500s
2		0.5M	210s
3		1M	100s
4	BIT-POP-75-OH-3.85 wt%	0.5M	1h20min
5	BIT-POP-75-OH-7.19 wt%	0.5M	30min

Table S8 Concentration of 4-NP and 4-AP and conversion rate during ten cycles of catalytic reduction

Cycle number	Concentration of 4-NP (ppb)	Concentration of 4-NP (mol/L)	Concentration of 4-AP (ppm)	Concentration of 4-AP (mol/L)	Conversion (%)
1	0.005174647	3.71982E-11	0.011029356	3.25228E-06	99.999
2	0.005171921	3.71786E-11	0.010529094	3.2484E-06	99.999
3	0.005185818	3.72785E-11	0.012807948	3.26607E-06	99.999
4	0.005193147	3.73312E-11	0.013957333	3.27499E-06	99.999
5	0.005186995	3.7287E-11	0.012444459	3.26325E-06	99.999
6	0.005207182	3.74321E-11	0.015581933	3.28758E-06	99.999
7	0.005188870	3.73005E-11	0.012670496	3.26501E-06	99.999
8	0.005198496	3.73697E-11	0.014317559	3.27778E-06	99.999
9	0.005176431	3.72111E-11	0.010359486	3.24709E-06	99.999
10	0.005212508	3.74704E-11	0.016882745	3.29767E-06	99.999

Table S9 Catalytic performance comparisons between Pd@BIT-POP-75-OH and other PdNPs for the reduction of 4-NP

heterogeneous catalysts	metal NPs loading (%)	metal NPs size(nm)	kapp (min^{-1})	time (min)	TOF (h^{-1})	ref
Pd@TP-POP	1.31	1.4-2.8	0.61	5.75	227.07	[1]
PtNPs@COF	34.4	--	--	8	56.4	[2]
Pd@PPM2	1.76	3.45	0.48	6	59.4	[3]
Pd@CHI	3.34	4.086	0.139	30	25.14	[4]
Pd/NHPC	3.22	4.45	0.37	8	122.40	[5]
Ag NPs@SCOF	0.95	20	1.06	3	81	[6]
Pd@DANI-CS-Fe3O4	3.5	3	0.22	14	228.69	[7]
Pd@h-mSiO2-4.9%	4.9	6	0.36	12.33	93.60	[8]
Pd@BIT-POP-75-OH	**12.53**	**4.25**	**0.967**	**3.5**	**175**	**This work**

6. Reference

[1] J. Yang, M. Yuan, D. Xu, H. Zhao, Y. Zhu, M. Fan, F. Zhang, Z. Dong, *J. Mater. Chem. A* **2018**, *6*, 18242-18251.

[2] S. Lu, Y. Hu, S. Wan, R. McCaffrey, Y. Jin, H. Gu, W. Zhang, *J. Am. Chem. Soc.* **2017**, *139*, 17082–17088.

[3] M. S. Bashir, X. Jiang, X. Z. Kong, *Eur. Polym. J.* **2020**, *129*, 109652.

[4] X. Li, F. Dong, L. Zhang, Q. Xu, X. Zhu, S. Liang, L. Hu, H. Xie, *Chem. Eng. J.* **2019**, *372*, 516-525.

[5] X. X. Wu, H. Zhou, *New. J. Chem.* **2017**, *41*, 10245-10250.

[6] N. Wang, F. Wang, F. Pan, S. Yu, D. Pan, *ACS Appl. Mater. Interfaces* **2021**, *13*, 3209-3220.

[7] M. M. Ayad, *Mol. Catal.* **2017**, *439*, 72-80.

[8] M. Tian, *J. Colloid Interface Sci.* **2018**, *521*, 132-140.