

# **A Soluble Porous Organic Polymer for Highly Efficient Organic-Aqueous Biphasic Catalysis and Convenient Reuse of Catalysts**

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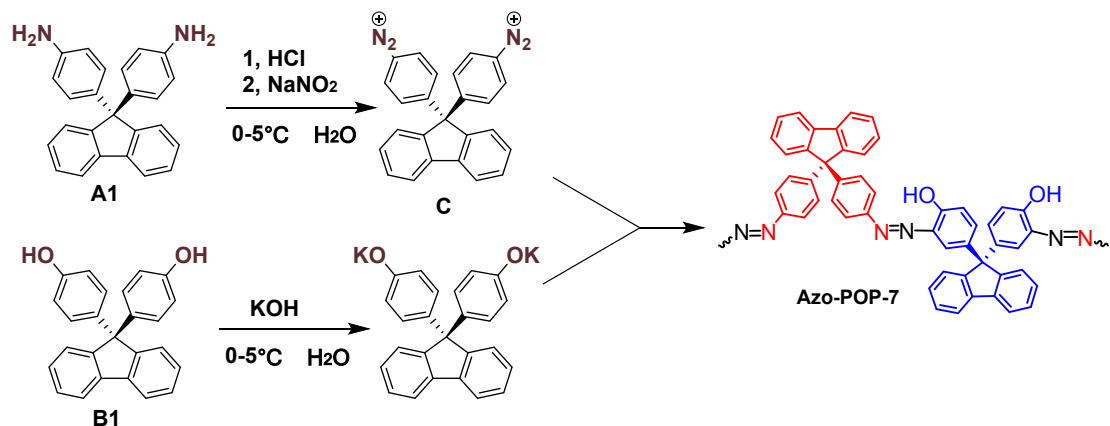
## General Information for materials and measurements:

All chemicals were purchased from commercial suppliers (Sinopharm Chemical Reagent Co.) and used without further purification, unless otherwise noted. The monomer of 9,9'-Bis(4-aminophenyl)fluorene (BAPF) were synthesized by modifying the reported methods<sup>[1]</sup>. Solution <sup>1</sup>H-NMR spectra were taken by Varian Mercury-400 MHz (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 100 MHz). 2D <sup>1</sup>H DOSY-NMR spectra were taken by Varian Mercury-400 MHz under constant temperature of 22 °C. The pulse sequence named 'Dbppste' was used for DOSY experiment with parameters as 'ss=-8', 'il='y'', 'bs=4', delflag='y', del=0.15s and gt1=0.004s. The concentration of the test samples was maintained at 1 mg/0.4ml, and chloroform-d6 was used as solvent. Diffusion coefficients (D) of polystyrene samples with known molecular weights (Mw) were obtained by DOSY. Thus, linear relationship between diffusion coefficients and molecular weights was fitted and calculated as  $\text{Lg}(D) = -0.54601 * \text{Lg}(Mw) - 7.81883$ . The diffusion coefficient of Azo-POP-7 was measured by DOSY. And its molecular weight (Mw) was calculate through the linear relationship between diffusion coefficients and molecular weights. Solid-state cross-polarization magic angle spinning (CP-MAS) <sup>13</sup>C-NMR spectra of solid samples were obtained using a Bruker Avance III 600 MHz Wide Bore spectrometer (14.2 T). A 4 mm MAS probe and ZrO<sub>2</sub> motor were used, and spin rates at 151 MHz. 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<sub>2</sub> 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 Tecnai G2 F30 transmission electron microscope (TEM) working at 300 kV. GPC was measured by waters 1515 Gel Permeation Chromatography instrument using DMF as the mobile phase with eluting rate of 1 ml/min, and monodisperse polystyrene standard sample was used to calibrate. N<sub>2</sub> adsorption/desorption studies were carried out at 77K

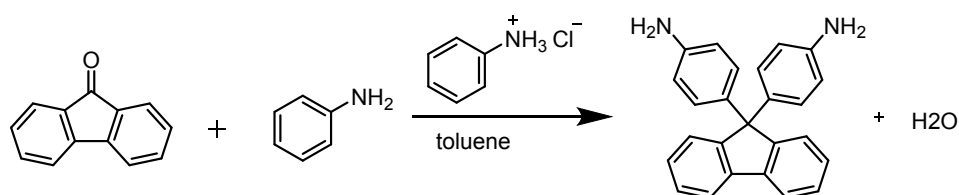
using the BELSORP-MAX-II (BEL, Japan, Inc., Japan). BET surface area and pore volume were obtained by Brunauer-Emmett-Teller (BET) method between the pressure range of 0.05-0.35  $P/P_0$ . Polymer pore size distributions were calculated from the adsorption branches using non-local density functional theory (NLDFT) methods.

## Syntheses of monomers and Azo-POP-7

### Synthesis of Azo-POP-7



### 9,9'-Bis(4-aminophenyl)fluorene (BAPF) (A1)



A mixture of 9-fluorenone (1.89 g, 10 mmol), aniline hydrochloride (1.94 g, 15 mmol), aniline (12 mL), and toluene (5 mL) were added to a 100 ml flask and then heated to flux with magnetic stirring for 4 h to remove the water by azeotropic distillation with toluene. After cooling to the room temperature, 35 mL 10% NaOH aqueous solution was added to the reaction solution, and was stirred for 0.5 h. The crude product was washed by cold methanol for two times. Then the BAPF was obtained by recrystallization using toluene, followed by drying under dynamic vacuum at room temperature for 24 h. (Yield: 40 %)

<sup>1</sup>H-NMR (400MHz, DMSO-d<sub>6</sub>) δ (ppm): 7.85 (d, 2H, H-Ar), 7.34–7.24 (m, 6H, H-Ar), 6.76 (d, 4H, H-Ar), 6.41 (d, 4H, H-Ar next to amino group), 4.92 (s, 4H, -NH<sub>2</sub>).

<sup>13</sup>C-NMR (100MHz, DMSO-d<sub>6</sub>)δ (ppm):152.77, 147.54, 139.77, 133.33, 128.69, 127.92, 127.43, 126.38, 120.66, 114.00, 64.05.

### Synthesis of Azo-POP-7

Firstly, 9,9'-Bis(4-aminophenyl)fluorene (1 mmol) was loaded in a 250 mL flat-bottomed flask charged with 100 mL of deionized water and 0.7 mL of concentrated hydrochloric acid. After stirred for 30 min at 0 °C, the mixture was added with 20 mL of aqueous solution of sodium nitrite (2.05 mmol) and stirred for 25 mins to make amino groups be completely converted to diazonium salts. If then some drops of fluorboric acid were added into the solution, the diazonium salts could be precipitated from solution and collected through filtration.

<sup>1</sup>H-NMR(400MHz, DMSO-d6) δ (ppm):8.60(d, 4 H), 8.09(d, 2 H), 7.72(d, 4 H), 7.56(t, 4 H), 7.44(t, 2 H).

Subsequently, the mixture was neutralized with dilute solution of KOH, and then mixed with 30 mL of aqueous solution of 9,9'-Bis(4-hydroxyphenyl)fluorene (1 mmol) and KOH (4 mmol) at 0~ 5 °C. After 12 h, solid precipitate was separated from the reaction mixture by filtration, and washed by the solvents in the order: water, aqueous 0.1M HCl, aqueous 0.1M KOH, water. After freeze drying, the polymer sample was obtained in a high yield of 88%.

Elemental Analysis: C (80.2%), N (7.41%), H (4.99%).

<sup>1</sup>H-NMR (400MHz, DMSO-d6) δ (ppm): 11.31 (s, -OH), 9.34 (s, -OH), 7.91-6.63 (m, H-Ar).

<sup>13</sup>C CP/MS NMR, δ (ppm): 150.92, 127.37, 119.45, 64.12.

FT-IR (cm<sup>-1</sup>): 3380(w), 3062(w), 2924(w), 2853(vw), 1596(m), 1491(s), 1448(s), 1279(m), 733(vs).

Elemental Analysis: C (80.2%), N (7.41%), H (4.99%).

2D <sup>1</sup>H DOSY-NMR: molecular weight (Mw) = 7639 g.mol<sup>-1</sup>

GPC measurement: molecular weight (Mw) = 7681 g.mol<sup>-1</sup>, PDI=2.1.

### **Loading of PdNPs on Azo-POP-7 to make the catalysts**

In a typical synthesis, 100 mg of Azo-POP-7 powder was dissolved in 17 mL CHCl<sub>3</sub>. Then, a CHCl<sub>3</sub> solution (2ml) containing different amounts (1mg for Pd@Azo-POP-7-1.0 and 2.5mg for Pd@Azo-POP-7-2.5) of palladium acetate was added and stirred for 3 h. Subsequently, different amounts (9 mg for Pd@Azo-POP-7-1.0 and 23 mg for Pd@Azo-POP-7-2.5) of NaBH<sub>4</sub> was dissolved in 1 ml of methanol and then was added into the CHCl<sub>3</sub> solution, followed by stirring for 3h. The final mixture was darker, but it was still clear solution. Then, the solution can be directly used for

subsequent catalytic reactions, or be dried by removing solvents.

### **Catalytic reduction reaction on 4-nitrophenol**

A 2 ml of the Pd@Azo-POP-7 in CHCl<sub>3</sub> solution and 4 mL of aqueous solution containing 4-NP and NaBH<sub>4</sub> was poured into the above solution, which was taken into a 10ml vial. The ratios of Pd@Azo-POP-7, 4-NP and NaBH<sub>4</sub> were listed in the Table S5. The solution was then stirred vigorously using a magnetic stirrer. Over a certain period of time, the reaction mixture was allowed to stand for several seconds. Then 10 μL solution was removed from the upper aqueous phase and diluted to 3 mL with water to take UV-vis measurements. The reaction was stopped when the absorption at 400 nm in the UV-vis spectra disappeared.

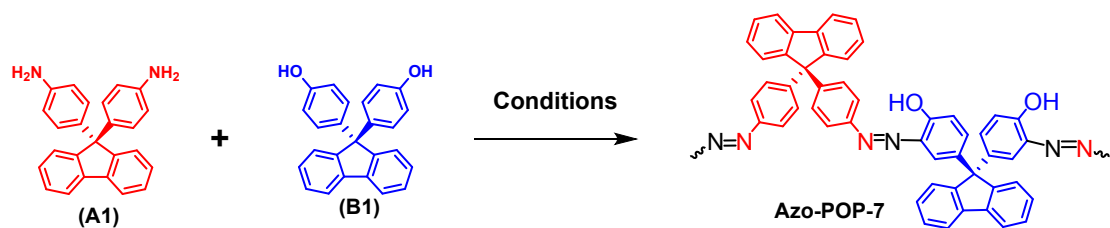
### **Separation and Reuse of the Pd@Azo-POP-7 catalyst**

When the reduction of 4-NP went completion, the biphasic solution was left standing for about 10 min until the 2 phases were completely separated. The stabilized PdNPs phase was separated by removing the upper aqueous layer. After the CHCl<sub>3</sub> phase was diluted to 4 mL with additional CHCl<sub>3</sub>, a new portion of aqueous 4-NP and NaBH<sub>4</sub> was added for the next run of reaction.



## Tables in ESI

**Table S1.** The optimization on the preparation of Azo-POP-7



Entry	Acid/Base	Solvents	Samples	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$
1	$\text{HBF}_4/\text{NaOH}$	Water	Azo-POP-7-a	132
2	$\text{HBF}_4/\text{NaOH}$	Acetonitrile/Water=4:1	Azo-POP-7-b	28
3	$\text{HBF}_4/\text{NaOH}$	THF/Water=4:1	Azo-POP-7-c	2
4	$\text{HCl}/\text{NaOH}$	Water	Azo-POP-7-d	260
5	$\text{HCl}/\text{KOH}$	Water	Azo-POP-7-e	364

**Table S2.** Elemental analysis of Azo-POP-7

Sample	Quality Percentage (%)							
	Found				Theoretical			
	N	C	H	C/N	N	C	H	C/N
AZO-POP-7	7.41	80.2	4.99	10.82	7.47	83.1	5.06	11.12

[a] Theoretical values were calculated assuming an ideal structure of Azo-POP-7 for the elemental analysis.

**Table S3.** Porosity Parameters for Azo-POP-7

Polymers	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{Lang}}/\text{m}^2 \cdot \text{g}^{-1}$	Mean diameter of pore/ nm	$V_{\text{total}}/\text{cm}^3 \cdot \text{g}^{-1}$
AZO-POP-7	364	496	19.38	1.76

**Table S4.** Solubility of Azo-POP-7 in different solvent

Solvent	Solubility of Azo-POP-7
DMF	Soluble
THF	Soluble
DMSO	Soluble
CHCl <sub>3</sub>	Soluble
3-Pentanone	Soluble
Dioxane	Soluble
Ethanol	Insoluble
Water	Insoluble
Pentane	Insoluble
Methanol	Insoluble
Ethyl acetate	Insoluble
Acetone	Insoluble
Acetonitrile	Insoluble

**Table S5.** The optimization on the conditions of catalytic reduction of 4-nitro phenol

Entry	CHCl <sub>3</sub> Phase (2ml)	Water Phase (4ml)	Reaction time for completely conversion
1	2mg Pd@AZO-POP-7-1.0	13.3 mg 4-NP; 260 mgNaBH <sub>4</sub>	1.9 min
2	2mg Pd@AZO-POP-7-1.0	13.3 mg 4-NP; 130mgNaBH <sub>4</sub>	4.5 min
3	2mg Pd@AZO-POP-7-1.0	13.3 mg 4-NP; 45 mgNaBH <sub>4</sub>	17.8 min
4	1mg Pd@AZO-POP-7-1.0	13.3mg 4-NP; 260 mgNaBH <sub>4</sub>	3.3 min
5	0.8mg Pd@AZO-POP-7-2.5	13.3 mg 4-NP; 260mgNaBH <sub>4</sub>	2.8 min
6	2mg AZO-POP-7-1.0	13.3 mg 4-NP; 260 mgNaBH <sub>4</sub>	No conversion after 1 h

**Table S6.** Comparison of  $k_{app}$  for 4-NP reduction over Pd@Azo-POP-7-1.0 with different reported catalyst systems.

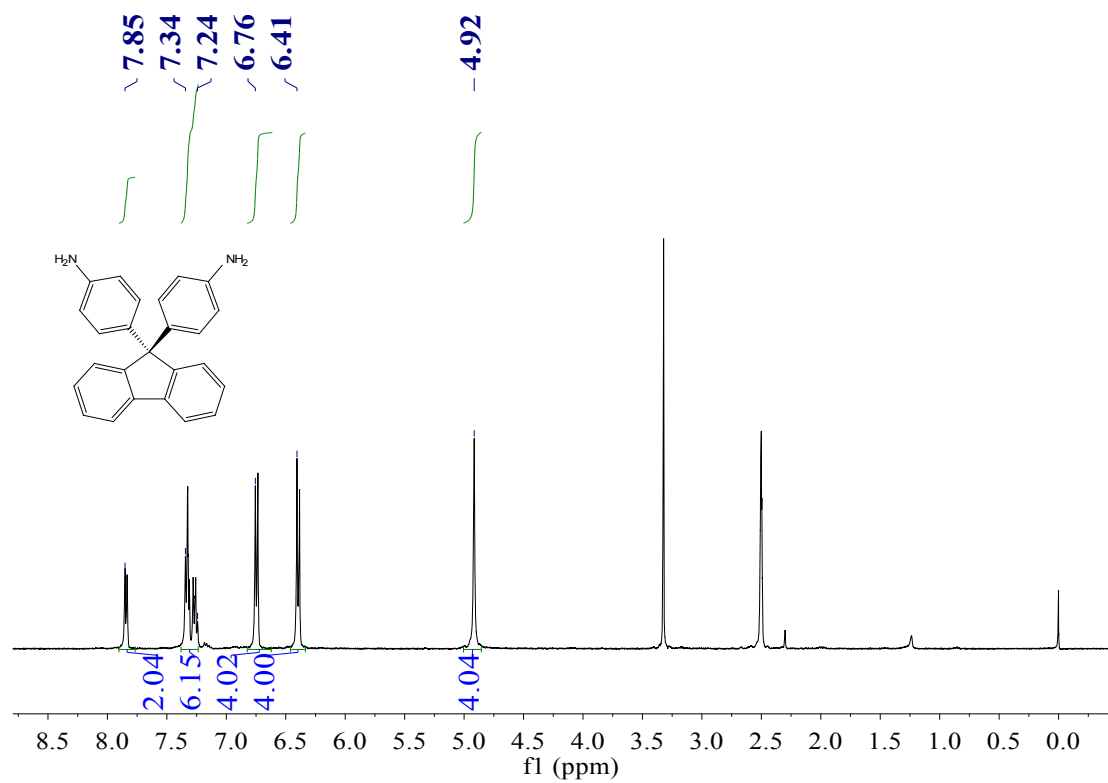
Entry	Catalyst	Biphasic solution	NaBH <sub>4</sub> /4-NP/Pd (mol/mol/mol)	$k_{app}/ 10^{-2}$ (s <sup>-1</sup> )	Reference
1	Au-PMMA	No	22500/15/1	0.72-0.79	2
2	Au-Poly(AG-co-VP)	No	51500/515/1	0.74	3
3	Au-PL-2	Yes	240000/1920/1	1.6	4
4	Au-PDI-2	Yes	240000/1920/1	2.7	4
5	Pd/Peptide	No	129/0.694/1	2.7	5
6	Pd-CNT/PiHP	No	2000/25/1	2.0	6
7	Pd-PAMAM	No	1000/10/1	0.359	7
8	Pd-SPB	No	1693/16.9/1	0.44	8
9	Pd-Microgel	No	833/8.3/1	0.15	8
10	Pd-HP2-OA	Yes	192000/1920/1	3.27	9
11	Pd@Azo-POP-7-1.0	Yes	38265/510/1	4.95	This work

Reference:

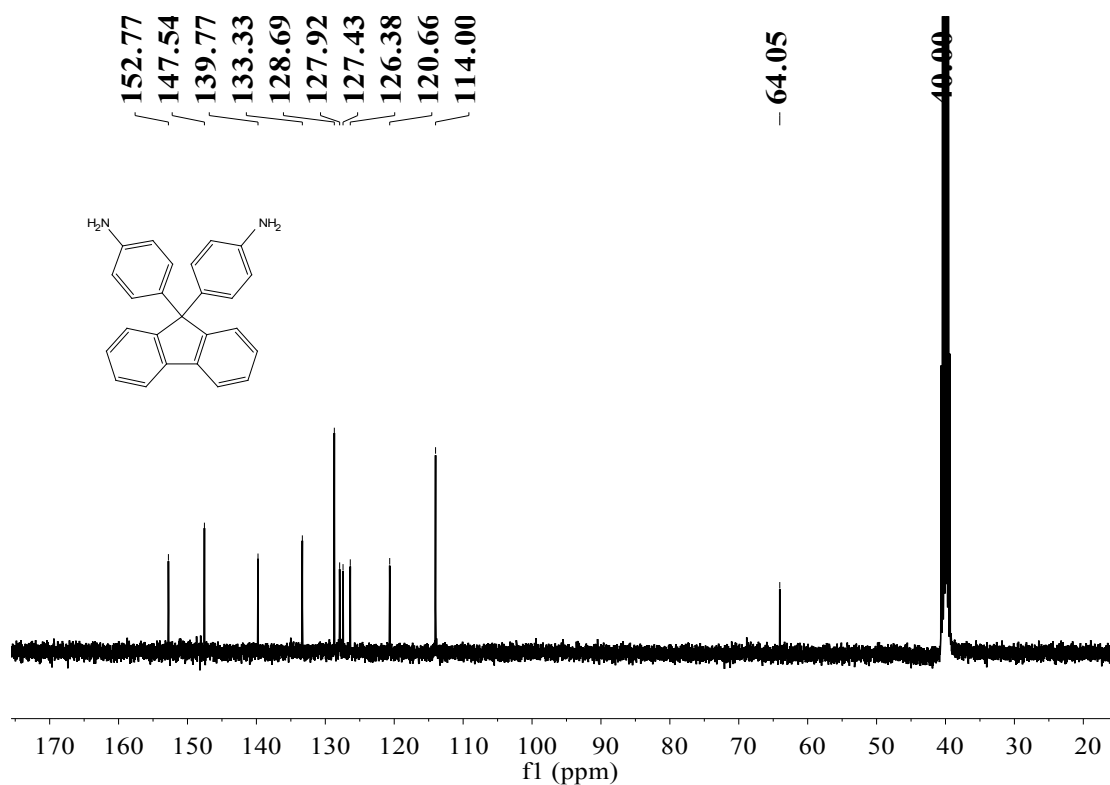
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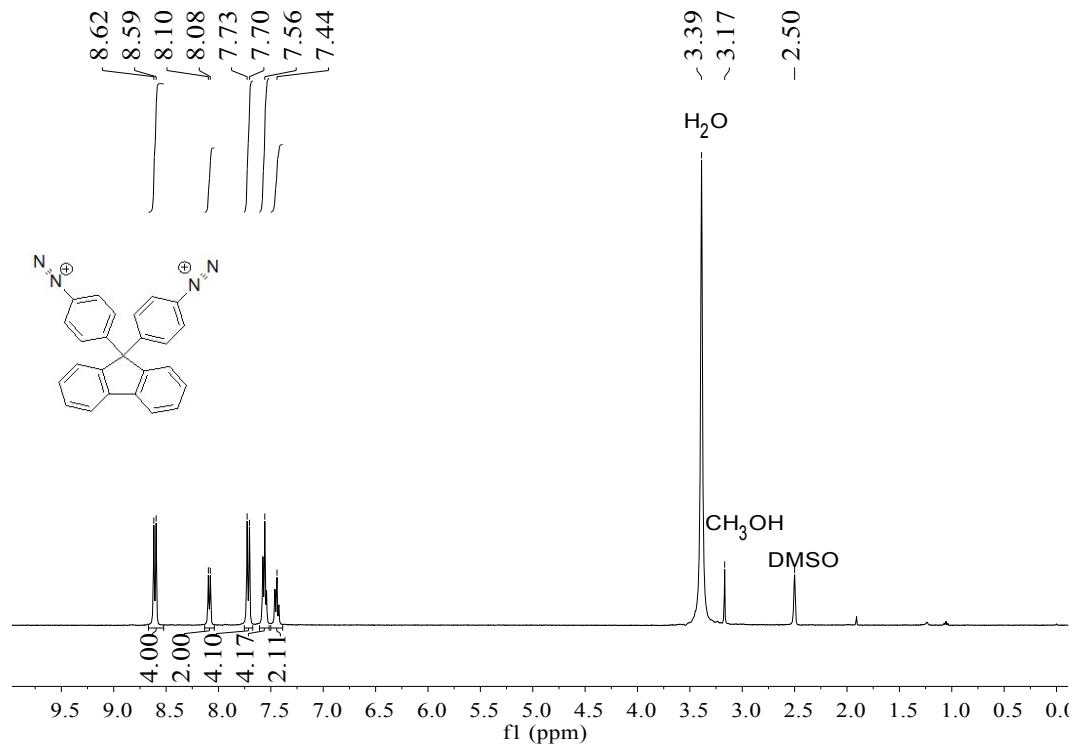
## Figures in ESI



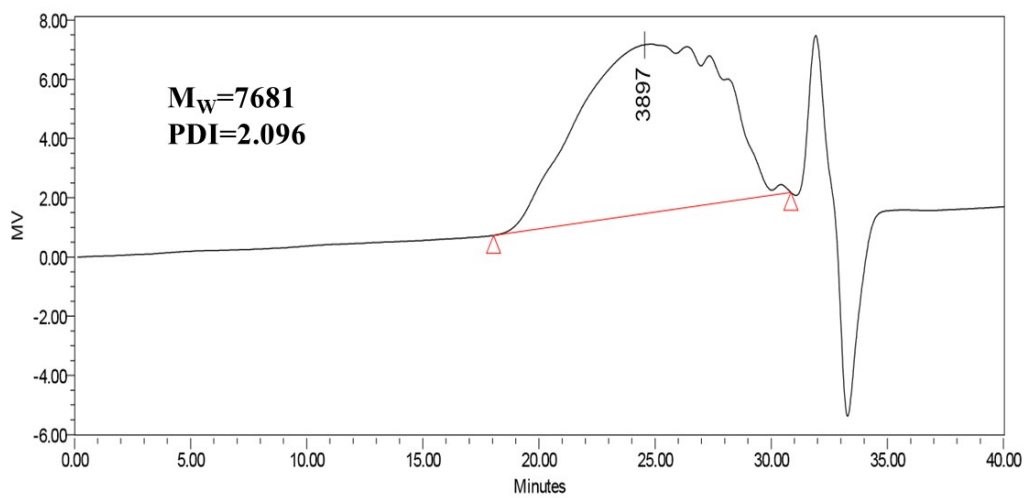
**Figure S1** <sup>1</sup>H-NMR spectra of 9,9'-Bis(4-aminophenyl)fluorene (BAPF) in DMSO-d<sub>6</sub>.



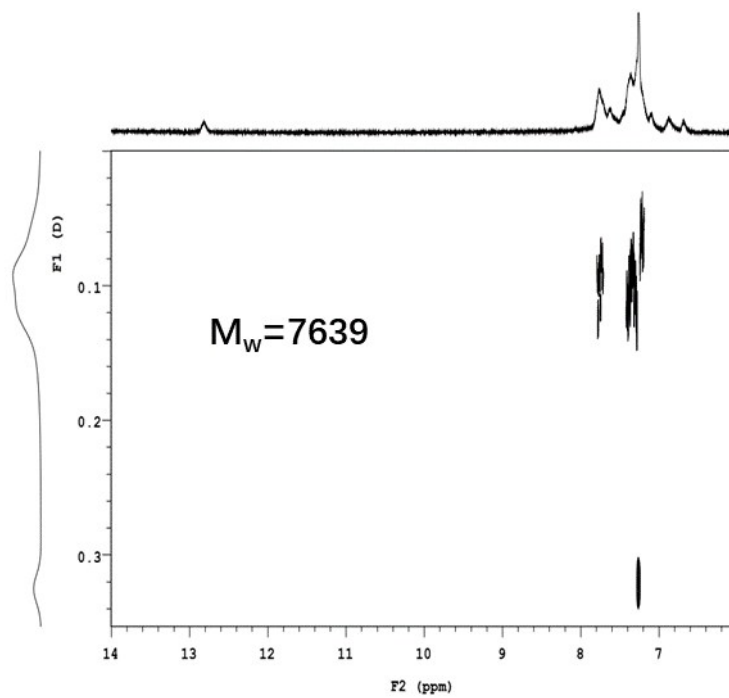
**Figure S2** <sup>13</sup>C-NMR spectra of 9,9'-Bis(4-aminophenyl)fluorene (BAPF) in DMSO-d<sub>6</sub>.



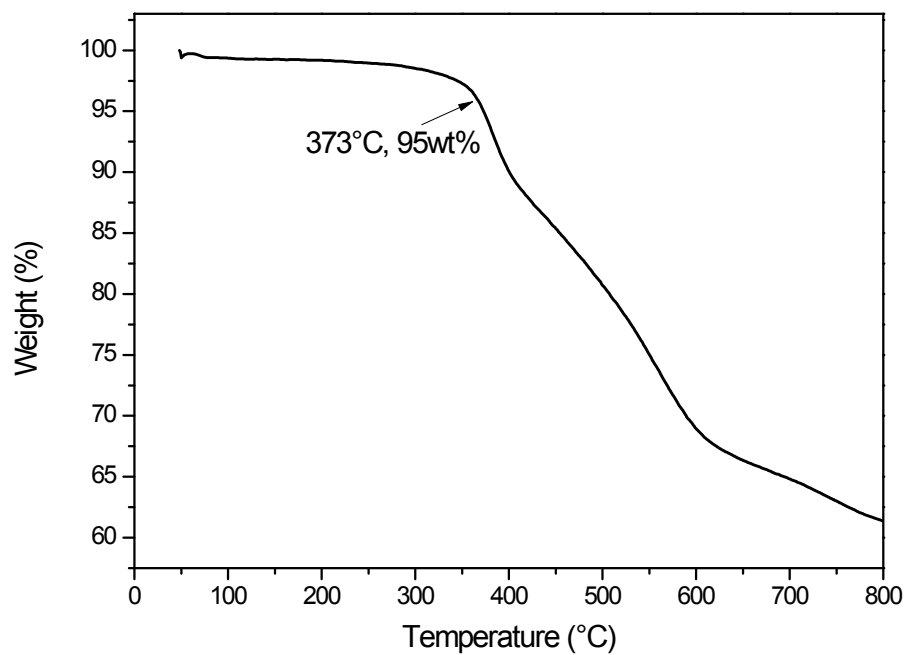
**Figure S3** <sup>1</sup>H-NMR spectra of diazonium salt of 9,9'-Bis(4-aminophenyl)fluorene (BAPF) in DMSO-d<sub>6</sub>.



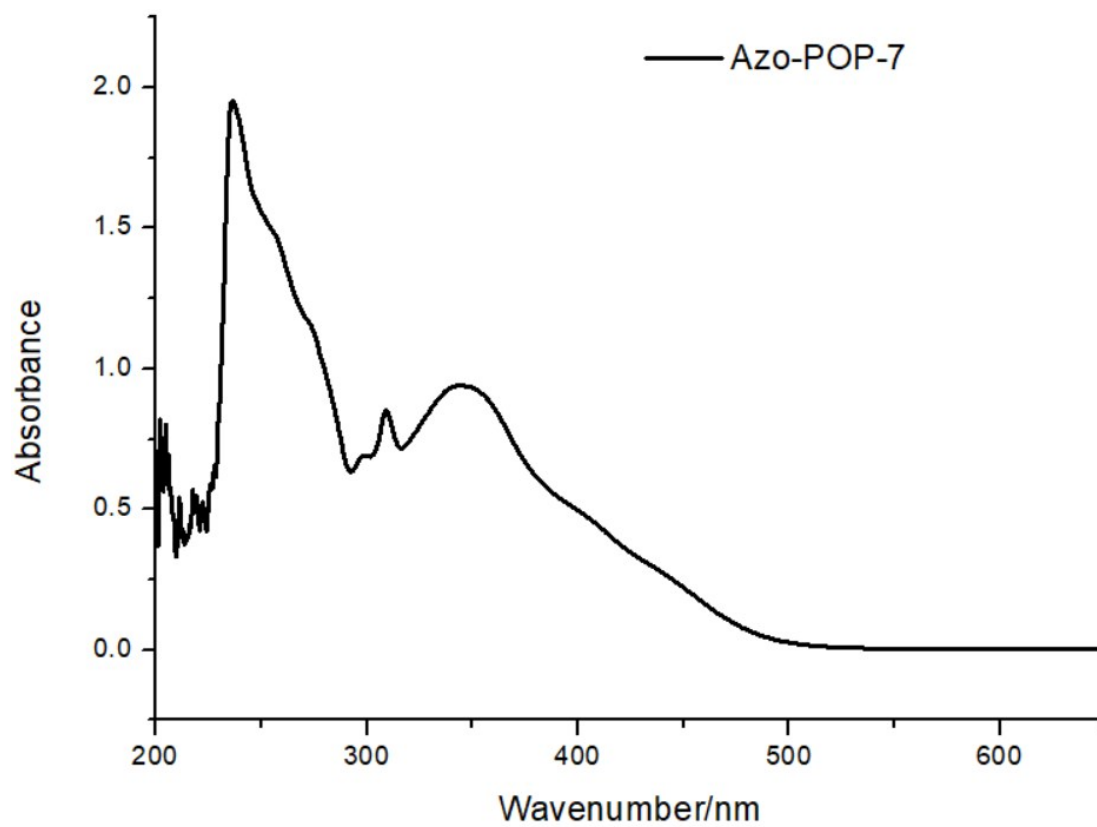
**Figure S4** Gel permeation chromatography(GPC) of Azo-POP-7



**Figure S5**  $^1\text{H}$ -DOSY-NMR of Azo-POP-7 in  $\text{CDCl}_3$

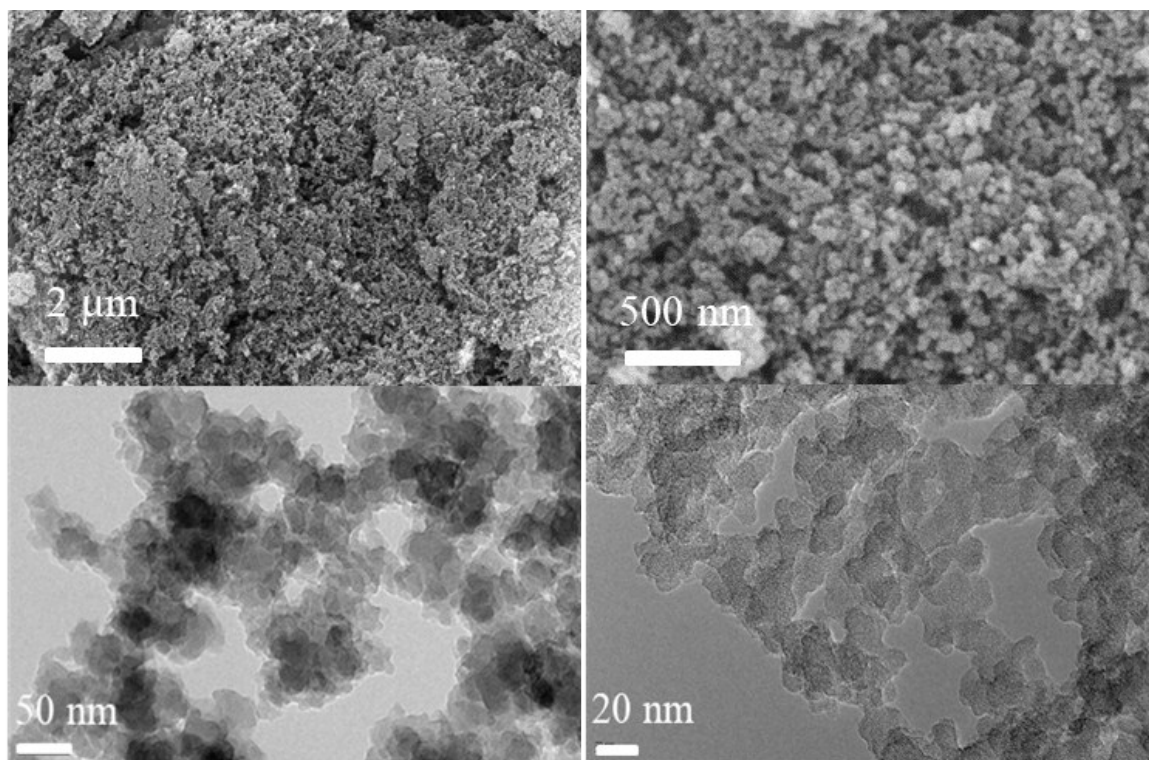


**Figure S6** TGA of Azo-POP-7

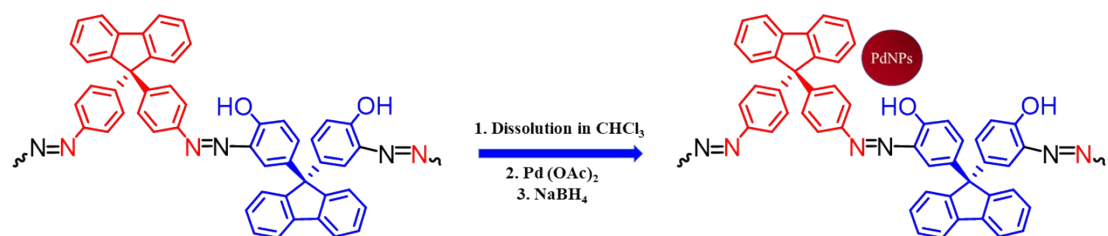


**Figure S7** UV/Vis spectrum of Azo-POP-7 in THF

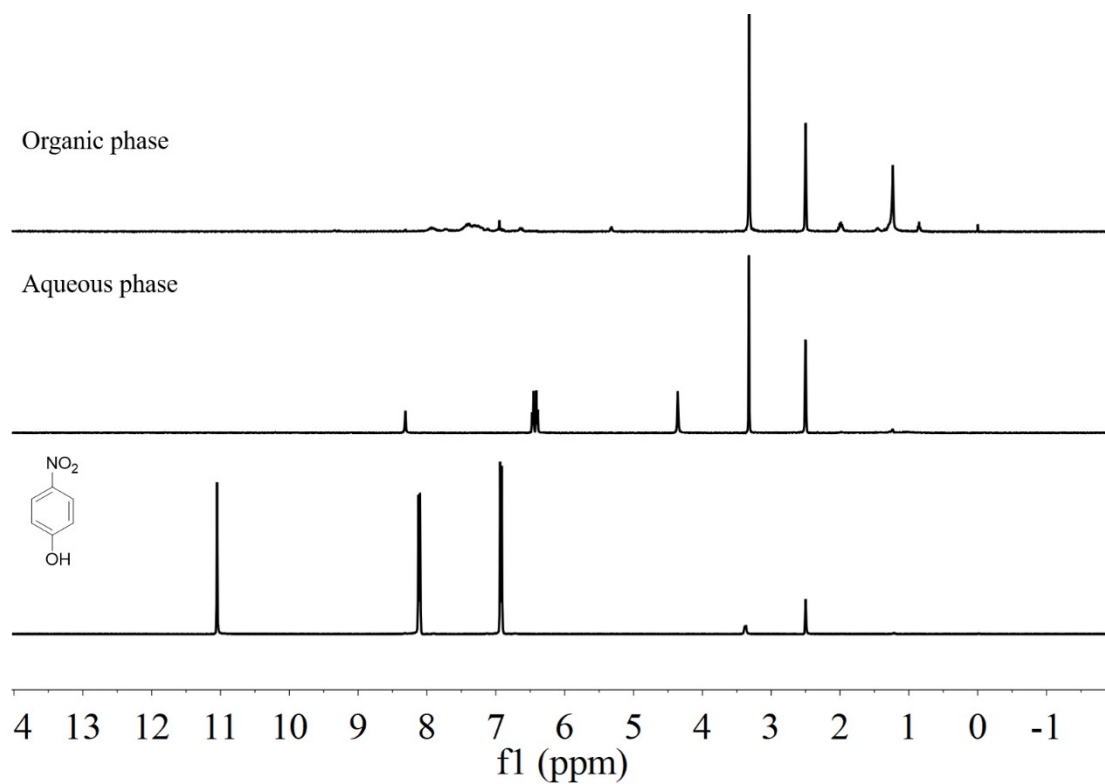




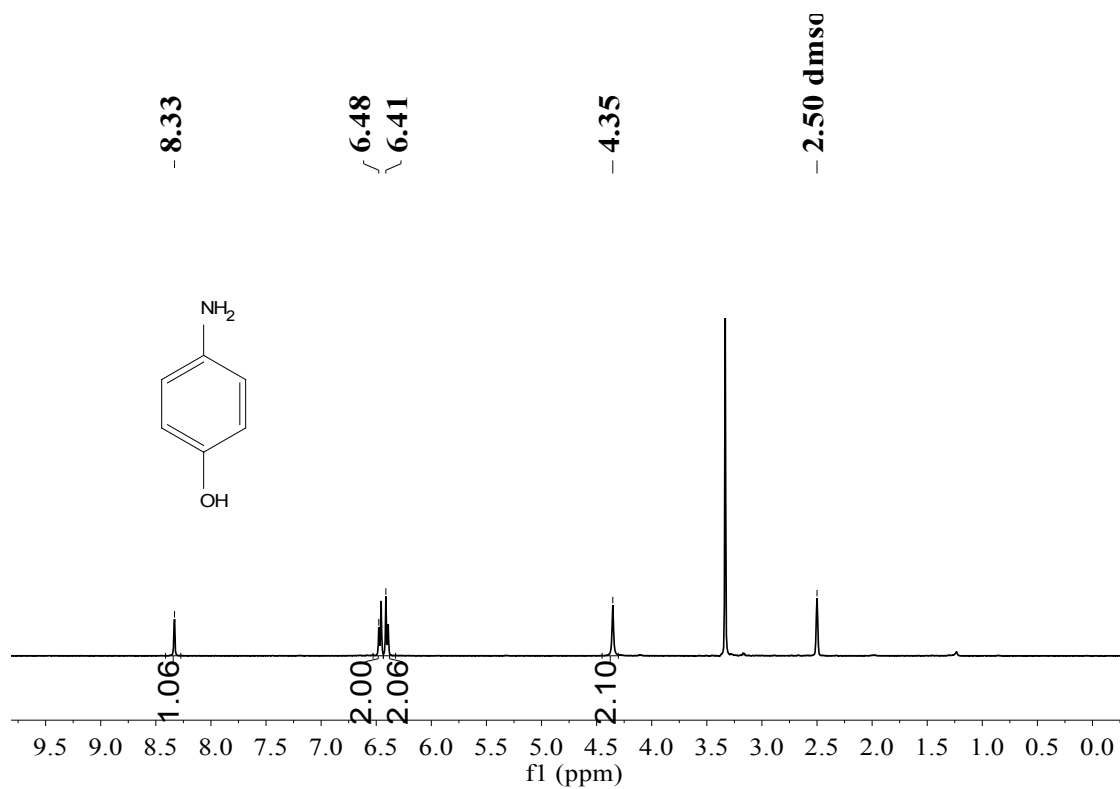
**Figure S8** SEM (top left and right) and HR-TEM (bottom left and right) images of Azo-POP-7.



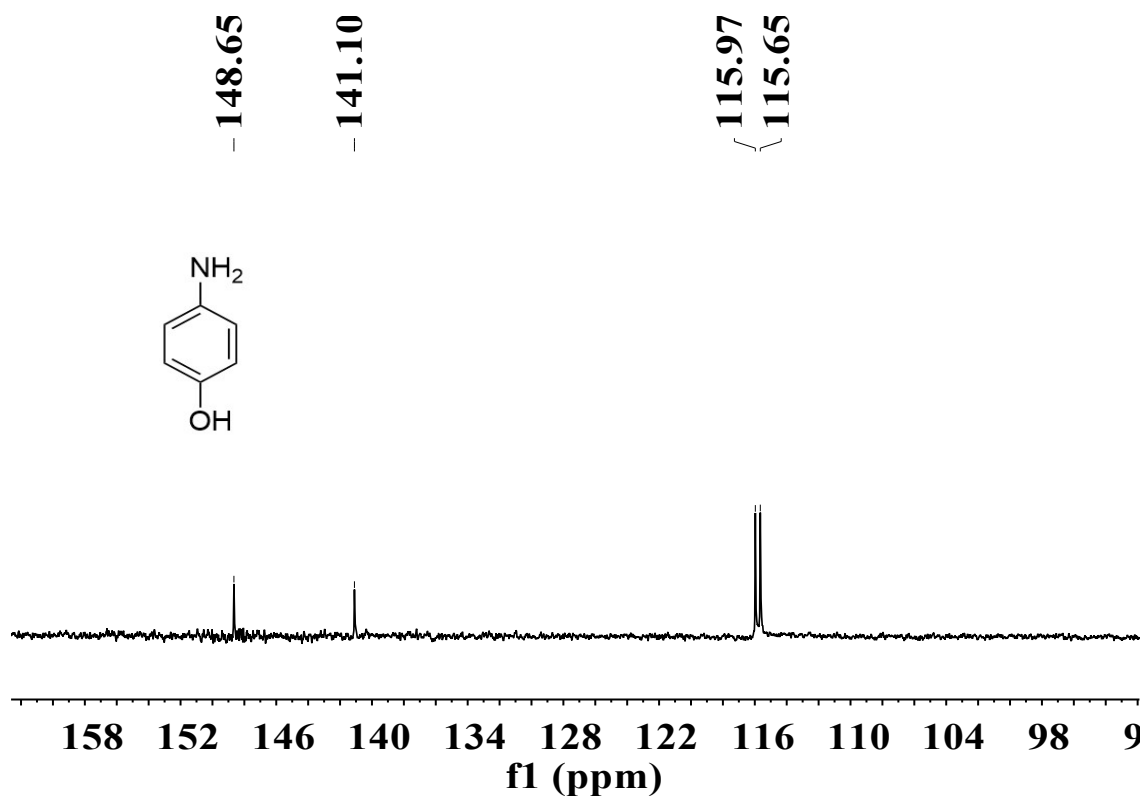
**Figure S9** Schematic illustration of the preparation of Pd@Azo-POP-7



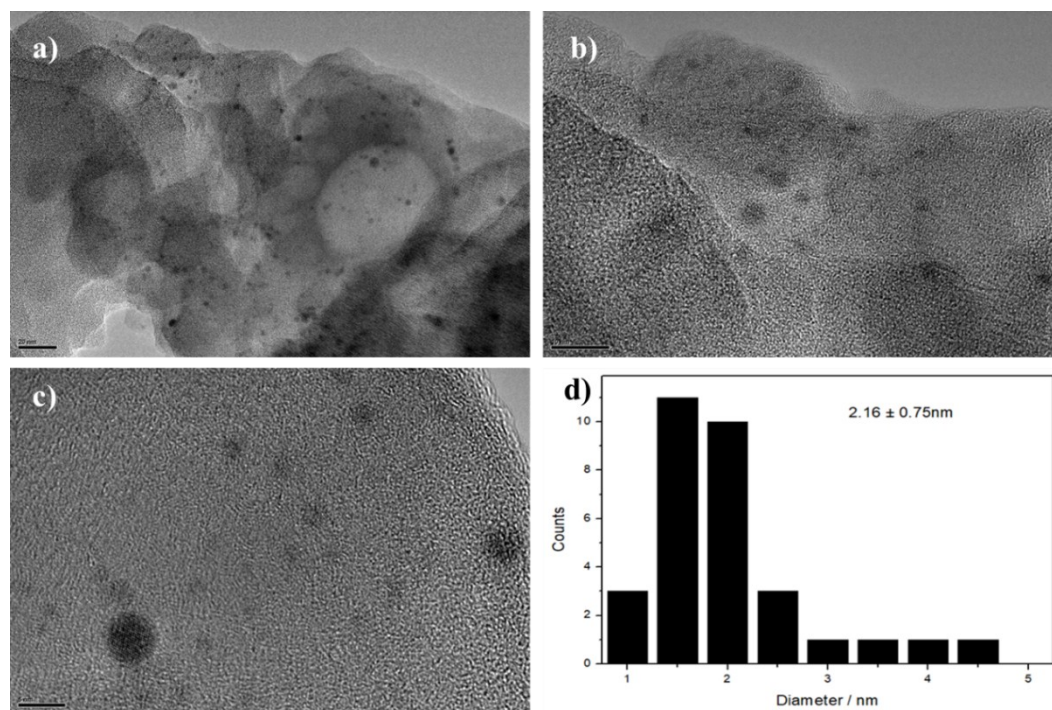
**Figure S10** Crude  $^1\text{H-NMR}$  (400MHz) spectra recorded in DMSO- $d_6$  of pure 4-nitrophenol, aqueous phase and organic phase after reaction.



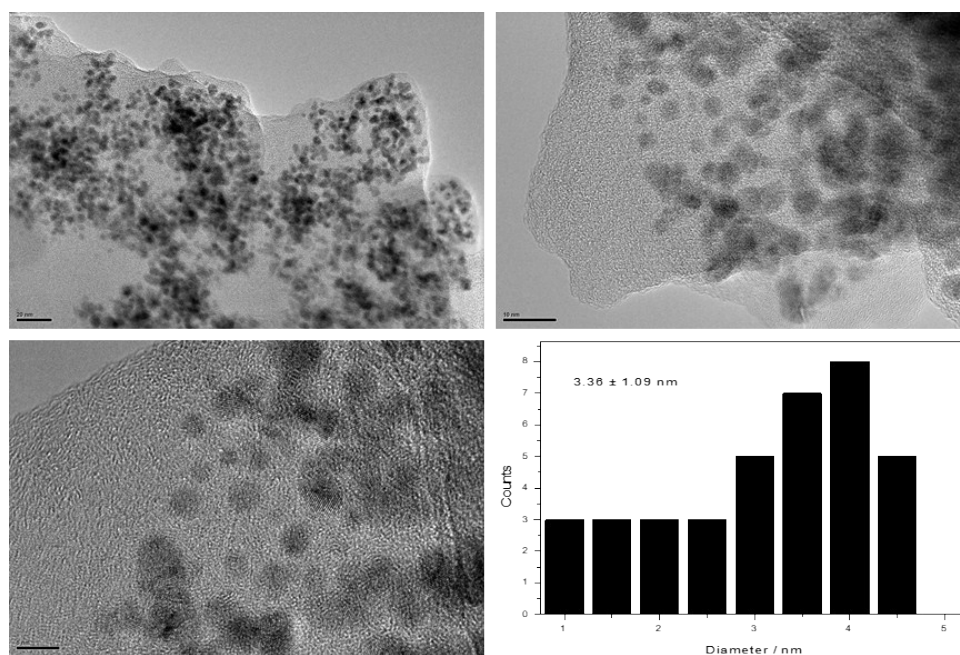
**Figure S11**  $^1\text{H-NMR}$  (400MHz) spectra of 4-amino phenol in DMSO- $d_6$ .



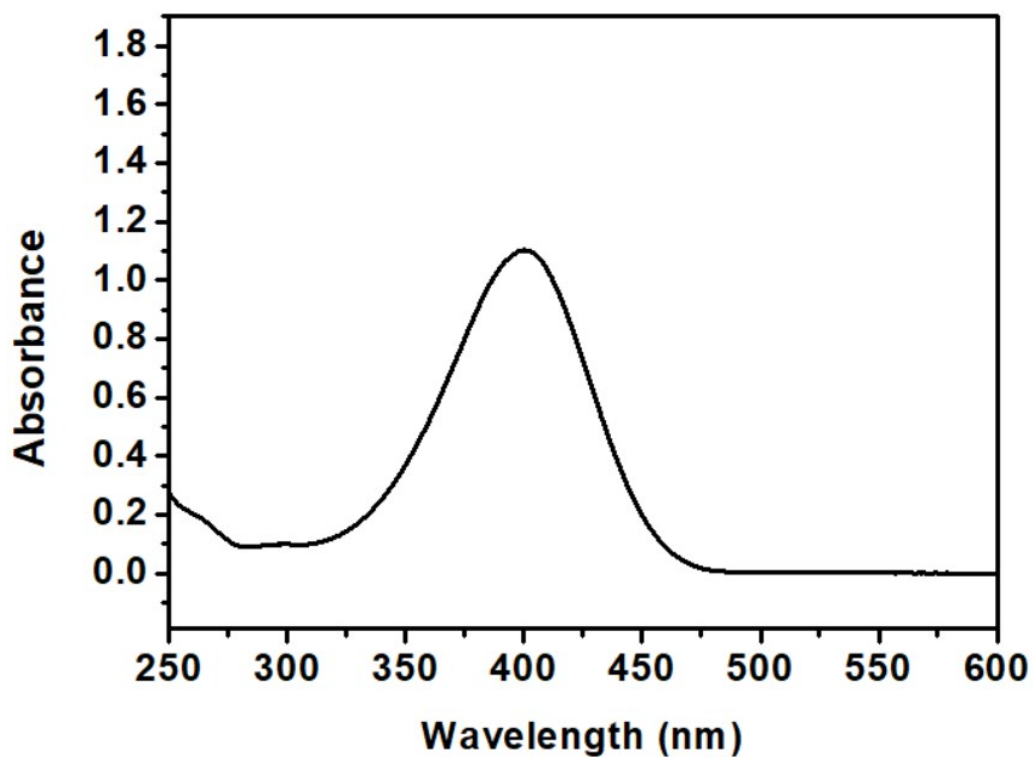
**Figure S12**  $^{13}\text{C}$ -NMR (400MHz) spectra of 4-amino phenol in DMSO-d<sub>6</sub>



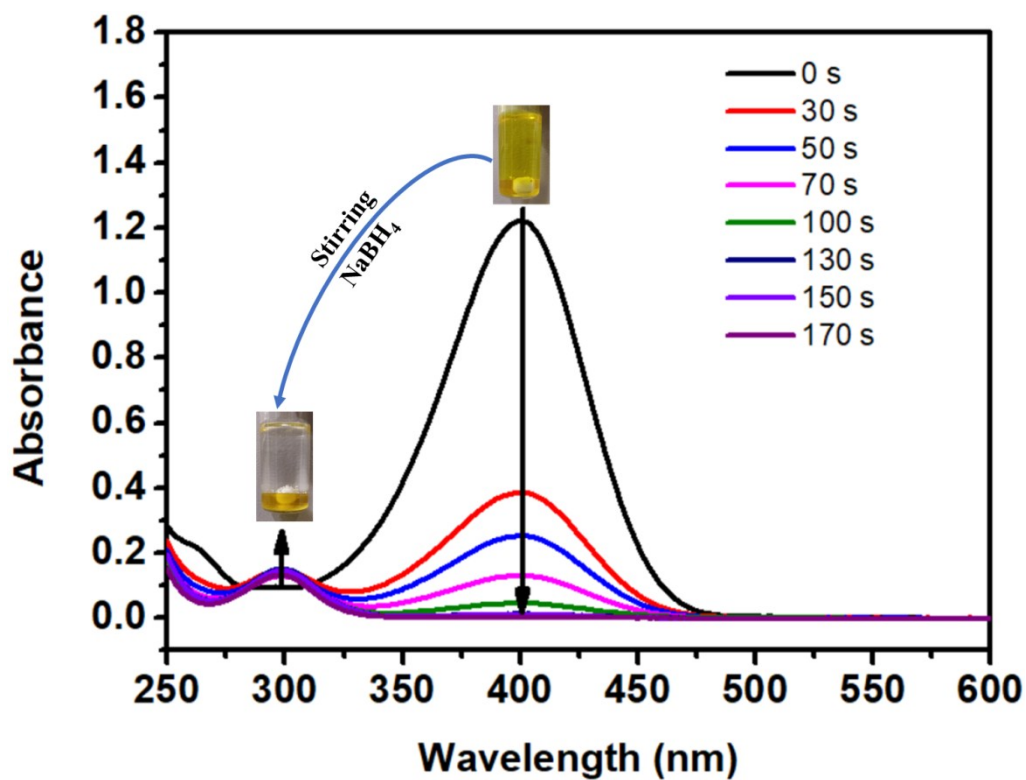
**Figure S13** TEM images and size distribution of Pd NPs of Pd@Azo-POP-7-1.0 (a) TEM, (b, c) HRTEM images and (d) the size distribution of Pd NPs with  $(2.16 \pm 0.75) \text{ nm}$ . Scale bars in a: 20 nm, b: 10 nm, c: 5 nm.



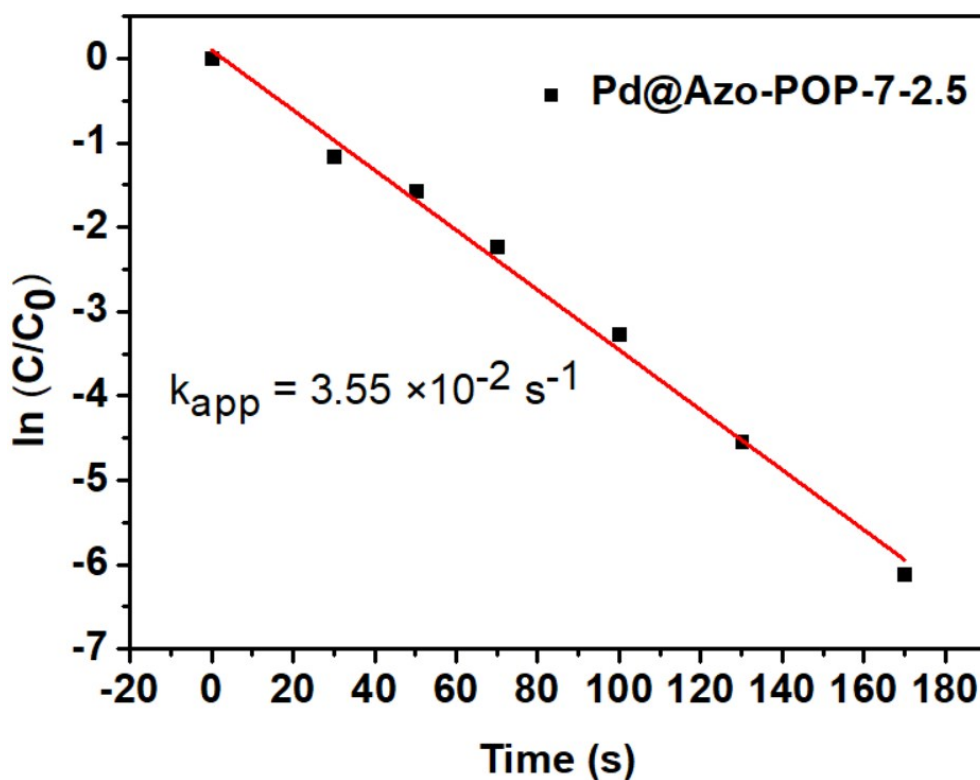
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**Figure S15** UV spectrum of the reduction reaction of 4-NP with  $\text{NaBH}_4$  catalyzed by Azo-POP-7-1.0



**Figure S16** UV spectrum of the reduction reaction of 4-NP with NaBH<sub>4</sub> catalyzed by Pd@Azo-POP-7-2.5



**Figure S17** Relationship between  $\ln(C/C_0)$  and reaction time of the reduction of 4-NP with NaBH<sub>4</sub> catalyzed by Pd@Azo-POP-7-2.5

## Reference

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