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Supporting Information

Do Polymer Ligands Block the Catalysis of Metal Nanoparticles? Unexpected Importance of the Binding Motifs Improving Catalytic Activity

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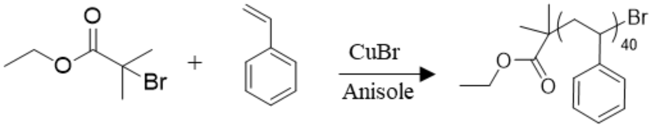
Additional Experimental Section

1. Chemicals and materials

Styrene (99%), anisole (anhydrous, 99.7%), N,N,N′,N′′,N′′ -pentamethyldiethylenetriamine (PMDETA, > 99%), Ethyl α-bromoisobutyrate (EBIB, 98%), copper(I) bromide (Cu(I)Br, 99.999% trace metal basis), dichloromethane (DCM, 99.9%), 1,4-dithiothreitol (DDT, ⩾ 97%), sodium citrate tribasic dihydrate (⩾99.0%), gold(III) chloride trihydrate ($HAuCl_4$, ⩾ 99.0%), palladium (II) chloride ($PdCl_2$, 99%), potassium hexachloroplatinate (IV) (K_2PtCl_6, 98%), oleylamine (97%), N-methyl imidazole (99%), dimethylformamide (DMF, 99.8%), methanol (99.8%), tetrahydrofuran (THF, anhydrous, ⩾ 99.9%), hexane (anhydrous, 95%), 4-nitrophenol, sodium borohydride ($NaBH_4$), dichloromethane (DCM, 99.9%), sodium iodide (NaI, 99.9%) and acetone (⩾ 99.5%) were all purchased from Sigma-Aldrich. Potassium carbonate (K_2CO_3, 99%) and benzyl alcohol (99%) were obtained from the Alfa-Aesar. Styrene was passed through an aluminum oxide column prior to use. The ultra-pure water was distilled with a High-Q distillation system (model # 103S).

2. Synthesis of Br-terminated PS (PS_{40}-Br)

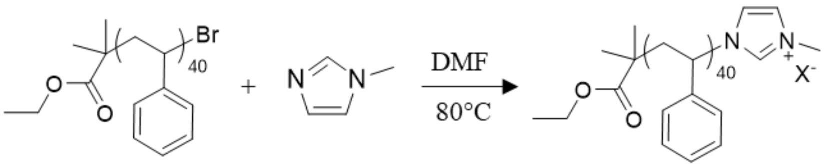
PS_{40}-Br was synthesized through atom transfer radical polymerization (ATRP) using ethyl α-bromoisobutyrate (EBIB) as an initiator. 38.41 mmol of styrene (4 g) and 0.96 mmol of Cu(I)Br (138 mg) were dissolved into 0.5 mL of anisole. The solution was purged with N_2 for 5 min, followed by an injection of 0.96 mmol of PMDETA (147 µL). The solution is purged once again for an additional 10 min. Afterwards, 0.96 mmol of EBIB (187 mg) that dissolved in 0.5 mL of anisole was added into the reaction system and the mixture was bubbled with N_2 for another 15 min. The polymerization was carried out at 80 °C for 30 min; and then the solution was cooled down to room temperature. An excess amount of dichloromethane (DCM) was added to quench the reaction. The reaction mixture was passed through a neutral alumina column to remove Cu(I)Br. The polymer was collected through precipitation with methanol three times and dried under vacuum. The numbers of repeat unit of styrene were calculated to be 40 based on end-group analysis using ^1H NMR peak (4.5 ppm). The resultant polymer has a $M_{n,\ SEC}$ of 8.2 kg mol^{-1} and Đ of 1.07, measured with a size exclusion chromatography (SEC) calibrated by polystyrene (PS).



Scheme S1. Synthesis of PS_{40}-Br.

3. Synthesis of PS_{40}-Imidazolium (PS_{40}-Im)

0.472 mmol of PS_{40}-Br (2 g), 9.42 mmol of *N*-methyl imidazole (0.774 g), 0.667 mmol of NaI (100 mg) were mixed in 5 mL of DMF. After purging with N_2 for 15 min, the reaction system was transferred to an oil bath and reacted at 80 °C for overnight. Finally, the polymer powder of PS_{40}-Im was precipitated with methanol three times and dried under vacuum.

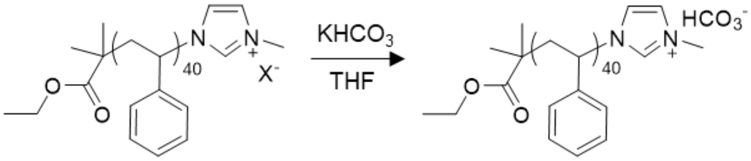


Scheme S2. Synthesis of PS_{40}-Im.

4. Synthesis of polystyrene-N-methylimidazolium bicarbonate (PS_{40}-Im HCO_3^-, P1) and polystyrene-N-heterocyclic carbene Cu(I) (PS_{40}-NHC Cu (I), P2)

4.1 Synthesis of P1 (PS_{40}-Im HCO_3^-)

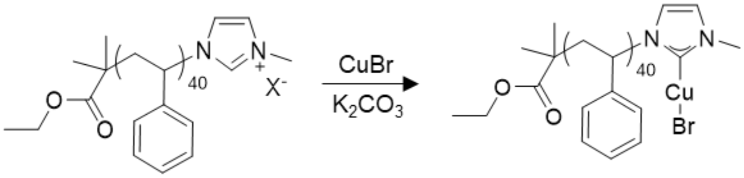
The anion exchange of PS_{40}-Im was carried through a previously reported method with some modification.[1] 0.024 mmol of PS_{40}-Im (100 mg) and 0.24 mmol of $KHCO_3$ (24 mg) were added into 2 mL of THF. After purging with N_2 for 5 min, the solution was stirred dramatically for two days at room temperature. Then, the reaction was cooled down with an ice bath to decrease the solubility of KBr in THF. After passing the solution through a silica column to remove KBr, the solution was precipitated with methanol three times to collect the polymer. The resultant polymer has a $M_{n,\,SEC}$ of 8.3 kg mol^{-1} and Đ of 1.08, measured from SEC calibrated by PS.



Scheme S3. Synthesis of P1.

4.1 Synthesis of P2 (PS_{40}-NHC Cu (I))

PS_{40}-Im (300 mg, 0.071 mmol), Cu(I)Br (30.4 mg, 0.21 mmol) and K_2CO_3 (29.3 mg, 0.21 mmol) were added into 125 mL of acetone. The above solution was refluxed at 80 °C for overnight under purging with N_2. The solution was cooled down to room temperature and passed through a silica column to remove the excess Cu(I)Br and K_2CO_3. Then, the polymer solution was concentrated using rotary evaporator and precipitated in methanol three times. The resultant polymer has a $M_{n,\,SEC}$ of 8.2 kg mol^{-1} and Đ of 1.07, measured from SEC calibrated by PS.



Scheme S4. Synthesis of P2.

5. Synthesis of thiol-terminated PS (PS_{40}-SH, P3)

P3 was synthesized through RAFT polymerization and reduction methods as reported previously.[2]

6. Synthesis of Au nanoparticles (AuNPs)

6.1 ~3 nm citrate (CA) capped AuNPs

4.9 mg of $HAuCl_4$ and 3.7 mg of sodium citrate was first dissolved in a 100 mL aqueous solution. Then, 1.5 mL of freshly prepared 0.1 M of $NaBH_4$ solution was added into above solution under stirring. The solution turned light orange immediately after adding $NaBH_4$ and was further stirred for 4 h. The final concentration of resultant ~3 nm AuNPs solution was 0.03 mg mL^{-1}.

6.2 ~14 nm CA capped AuNPs

~14 nm CA capped AuNPs were synthesized according to the previous reported method.[3] Typical, 100 mg of $HAuCl_4$ was added into 500 mL of H_2O and heated to boiling under stirring. 30 mL of sodium citrate (1 wt%) aqueous solution was then quickly injected into the above solution. After refluxing for 30 min, 0.1 mg mL^{-1} of AuNPs was collected as a stock solution without further purification.

6.3 ~33 or ~44 nm CA capped AuNPs

10 mg of $HAuCl_4$ was dissolved into 500 mL of H_2O and heated to boiling under stirring. 3 mL of sodium citrate (1 wt%) solution was then quickly injected into above solution. Followed by reflux for 30 min, the reaction temperature was decreased to 85 °C. Another 10 mg of $HAuCl_4$ and 3 mL of sodium citrate (1 wt%) solution were quickly injected in sequence to the solution. Repeat this step every 15 min for 7 times (70 mg of $HAuCl_4$ and3 mL of sodium citrate in total) will yield the ~33 nm AuNPs (0.09 mg mL^{-1}). In similar way, repeat this step every 15 min for 15 times will produce the ~44 nm AuNPs (0.17 mg mL^{-1}).

6.4 ~12 nm oleylamine (OAm) capped AuNPs

40 mg $HAuCl_4$ was added into a mixture of 6 mL of benzyl alcohol and 3 mL of oleylamine, this mixture was then heated to 120 °C for 20 min. After cooling down to the room temperature, the OAm capped AuNPs (Au-OAm) were collected by precipitation with excess acetone and finally stored in hexane (0.3 mg mL^{-1}).

7. Synthesis of Pd and Pt nanoparticles

7.1 CA capped Pd nanoparticles (PdNPs)

PdNPs were synthesized according to the previous report.[4] 9.4×10^{-4} M solution of $PdCl_2$ was prepared by first dissolving the 17 mg of $PdCl_2$ in 2 mL of 1 mol/L HCl and then filling with H_2O to 100 mL. 7.5 mL of $PdCl_2$ solution (9.4×10^{-4} M) and 15 mL of sodium citrate (1 wt%) were added into 52.5 mL of H_2O under string and then heated to reflux for 21 h. After cooling down to the room temperature, 0.01 mg mL^{-1} of PdNPs was stored as a stock solution without further purification.

7.2 CA capped Pt nanoparticles (PtNPs)

1 mL of K_2PtCl_6 (16 mM) and 1 mL of sodium citrate (40 mM) were added into 38 mL of H_2O then it was further stirred for 30 min at room temperature. Followed by injecting 200 µL of $NaBH_4$ (50 mM), the mixture was further proceeded for 1 h under stirring. Finally, 0.08 mg mL^{-1} of PtNPs was stored as a stock solution for further use.

8. Estimation of the grafting density

The following equation is employed to calculate the numbers of polymer chains per NP.

$$\text{Polymer chains /Au NPs} = \frac{\text{Number of polymers}}{\text{Surface area of an AuNP}\times\text{Number of AuNPs}} = \frac{m_P/M_P \times N_A}{S_{NP}\times\frac{m_{Au}/M_{Au}}{\rho_{Au}\times\frac{V_{NP}}{M_{Au}}}}$$

Where M_p and M_{Au} are the molecular weights of polymer and Au atom, respectively; m_p and m_{Au} are the mass of polymer and AuNPs, respectively; ρ_{Au} is the density of bulk Au; S_{NP} and V_{NP} are the surface area and the volume of an individule AuNP, respectively; and N_A is the Avogadro constant.

As shown in TGA in Figure S6, the weight loss of 92.1 wt%, 94.1 wt% and 97.8 wt% were measured respectively from the thermal decomposition of P1, P2, and P3 with respect to their initial mass.

To calculate the grafting density of P1 on ~14 nm AuNPs, 2.72 mg of Au-P1 was employed for TGA experiments. Two TGA experiments were carried out for unmodified Au and Au-P1. Unmodified AuNPs shows a loss weight of 0 wt%. The weight loss of Au-P1 is 5.2 wt% at 700 ºC. This gives the weight ratio of P1, (5.2 wt%-0 wt%)/92.1 wt% =5.6 wt%. Thus, the grafting mass of P1 on Au-P1 is 0.15 mg. The mass of AuNPs is 2.57 mg.

Thus, the grafting density of P1 on Au = $\frac{0.15\ \mathrm{mg}/4500\ \mathrm{g\ mol^{-1}} \times 6.023\times10^{23}\ \mathrm{mol^{-1}}}{615\ \mathrm{nm^2} \times \frac{2.57\ \mathrm{mg}/196\ \mathrm{g\ mol^{-1}}}{19.3\ \mathrm{g\ cm^{-3}} \times \frac{1.436\times10^{-24}\ \mathrm{m^3}}{196\ \mathrm{g\ mol^{-1}}}}}$ = 0.35 chains/nm^2

Similarly, to calculates the grafting density of P2 on ~14 nm AuNPs, 1 mg of Au-P2 was used for TGA experiments. Two TGA experiments were carried out for unmodified Au and Au-P2. Unmodified Au was used as the blank to subtract the background, which shows a loss weight of 0 wt%. The weight loss of Au-P2 is 4.23 wt% at 700 ºC. This gives the weight ratio of P2, (4.23 wt%-0 wt%)/94.1 wt% =4.5 wt%. Thus, the grafting mass of P2 is 0.045 mg. The mass of Au NPs is 0.955 mg.

The total number of P2 chains grafted on Au is, $m_{P2}/M_{P2}\times N_A$=0.045 mg/4500 g mol$^{-1}\times6.023\times10^{23}$ mol^{-1} =6.02×10^{15}

The mass of Au (0.71 mg) was used to calculate the total number of Au NPs for the TGA measurements. The number of AuNPs is $\frac{m_{Au}/M_{Au}}{\rho_{Au}\times\frac{V_{NP}}{M_{Au}}} = \frac{0.955\ \mathrm{mg}/196\ \mathrm{g\ mol^{-1}}}{19.3\ \mathrm{g\ cm^{-3}}\times1.436\times10^{-24}\ \mathrm{m^3}/196\ \mathrm{g\ mol^{-1}}}$ =3.43×10^{13}

The average diameter (r) of AuNPs is ~14 nm calculated from TEM image. Thus, surface area of an individual AuNP (S_{NP}) =$4\pi r_{Au}^2=4\times3.14\times(7\times10^{-9}\ \mathrm{m})^2=6.15\times10^{-16}\ \mathrm{m^2}$=615 nm^2

So, the grafting density of P2 on Au = $\frac{6.02\times10^{15}}{615\ \mathrm{nm^2}\times3.43\times10^{13}}$ =0.29 chains/nm^2

In addition, to calculate the grafting density of P3 on ~14 nm AuNPs, 1 mg of Au-P3 was employed for TGA experiments. Unmodified AuNPs shows a loss weight of 0 wt%. The weight loss of Au-P3 is 3.6 wt% at 700 ºC. This gives the weight ratio of P1, (3.6 wt%-0 wt%)/97.8 wt% =3.7 wt%. Thus, the grafting mass of P3 on Au-P3 is 0.037 mg. The mass of AuNPs is 0.963 mg.

Thus, the grafting density of P3 on Au = $\frac{0.037\ \mathrm{mg}/5240\ \mathrm{g\ mol^{-1}} \times 6.023\times10^{23}\ \mathrm{mol^{-1}}}{615\ \mathrm{nm^2} \times \frac{0.963\ \mathrm{mg}/196\ \mathrm{g\ mol^{-1}}}{19.3\ \mathrm{g\ cm^{-3}} \times \frac{1.436\times10^{-24}\ \mathrm{m^3}}{196\ \mathrm{g\ mol^{-1}}}}}$ = 0.20 chains/nm^2

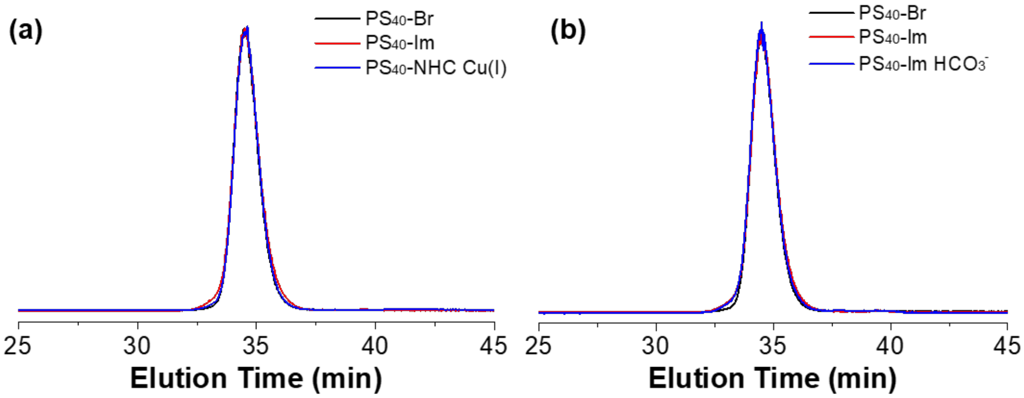


Figure S1. SEC elution curves of (a) PS_{40}-Br, PS_{40}-Im, PS_{40}-NHC Cu (I) and (b) PS_{40}-Br, PS_{40}-Im, PS_{40}-Im HCO_3 measured in THF.

Table S1. Summary of molecular weights and dispersity indexes of different polymers measured from SEC.

Polymers	$M_{n,\ NMR}$ (kg/mol)	$M_{n,\ SEC}$ (kg/mol)	Đ (M_w /M_n)
PS_{40}-Br	4.4	8.2	1.07
PS_{40}-Im	4.4	8.1	1.09
PS_{40}-NHC Cu (I)	4.5	8.2	1.07
PS_{40}-Im HCO_3^-	4.5	8.3	1.08

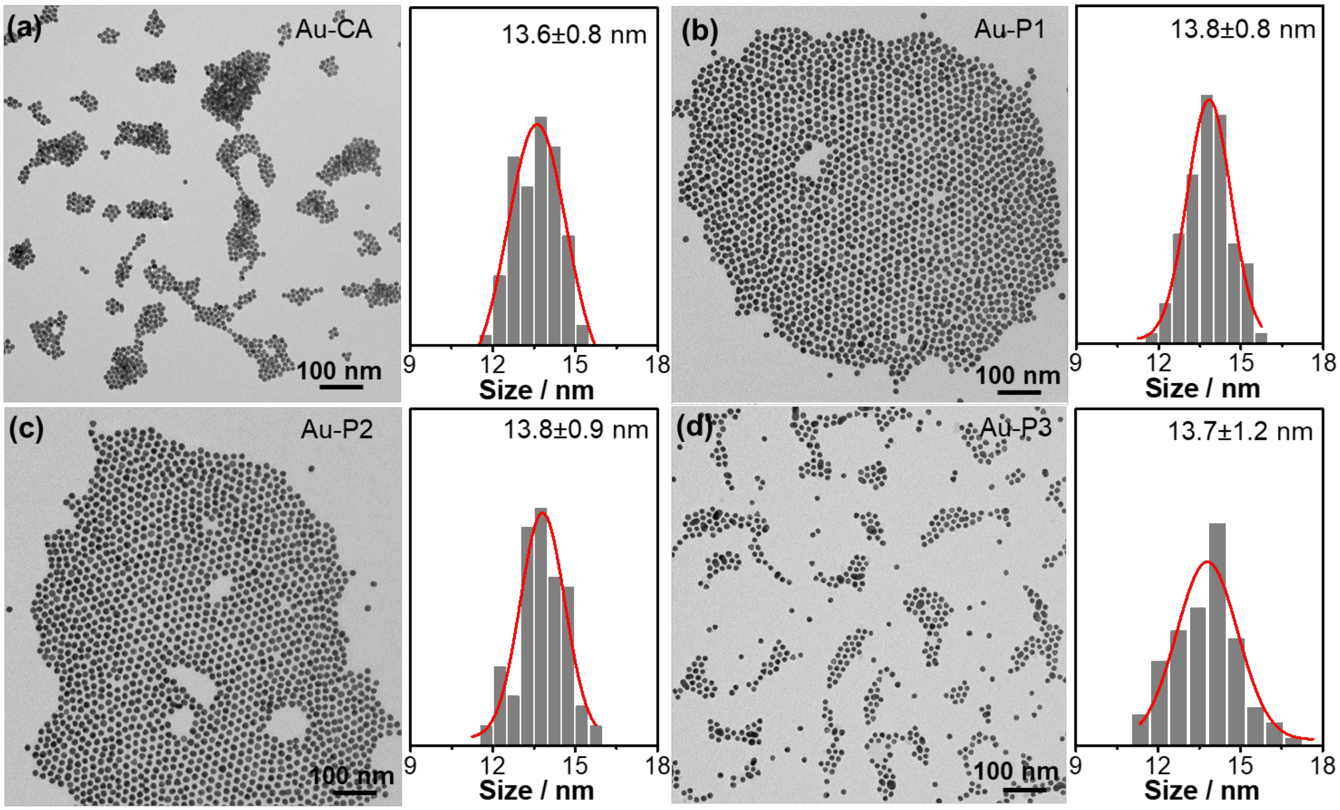


Figure S2. TEM images and corresponding size distribution of (a) Au-CA, (b) Au-P1, (c) Au-P2 and (d) Au-P3. All the Au NPs used here have an average diameter of ~14 nm.

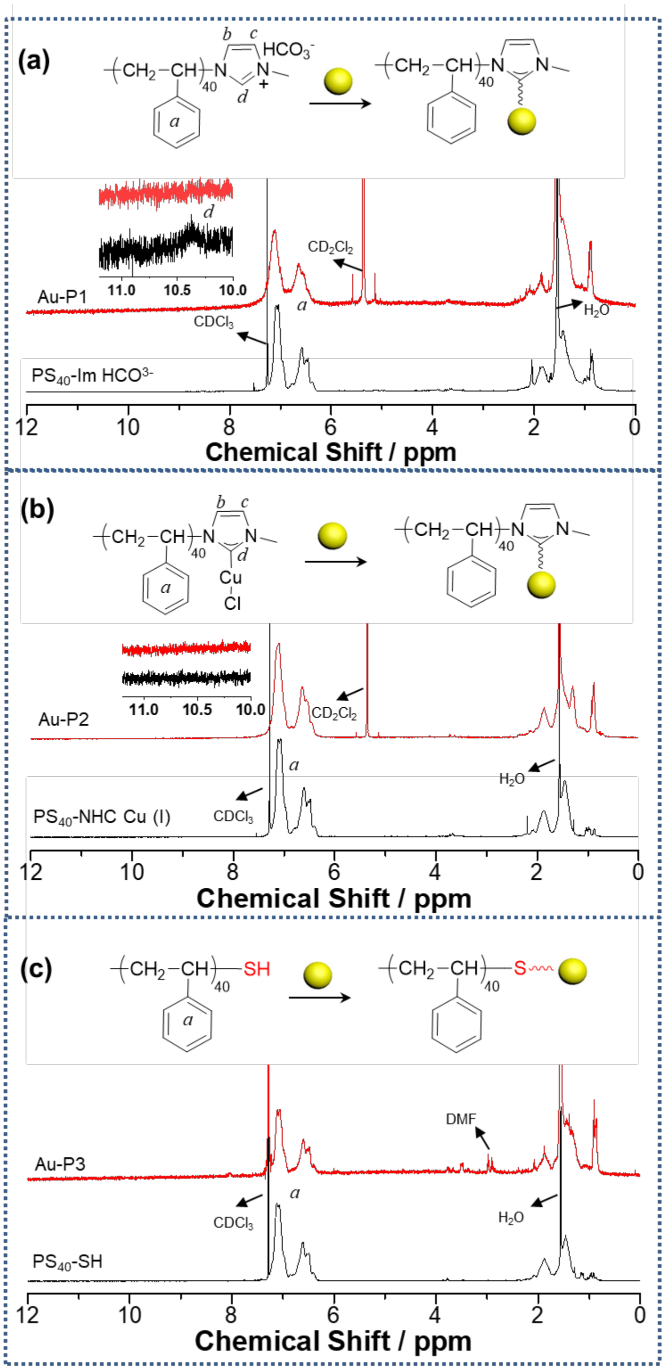


Figure S3. ^{1}H NMR spectra of (a) P1, (b) P2 and (c) P3 before and after modification with AuNPs. The solvent peaks in NMR spectra were labeled with black arrows.

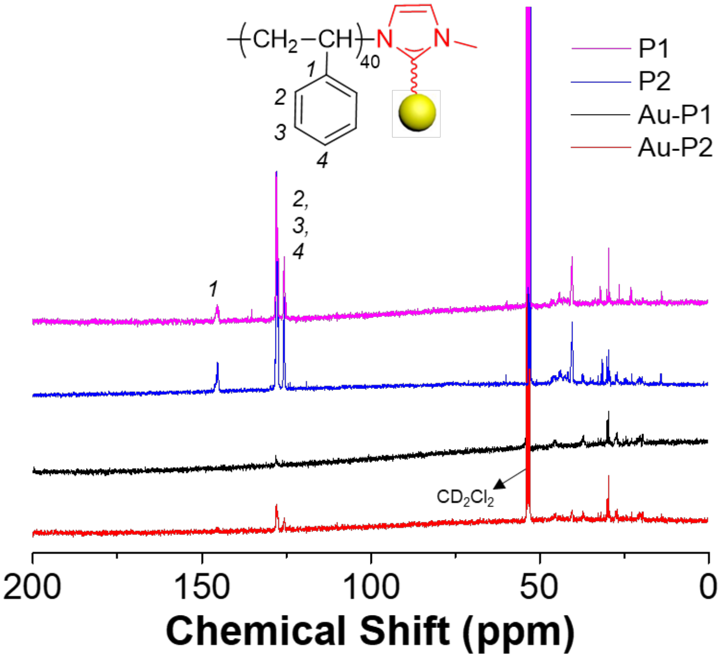


Figure S4. ^{13}C NMR spectra of P1, P2, Au-P1 and Au-P2.

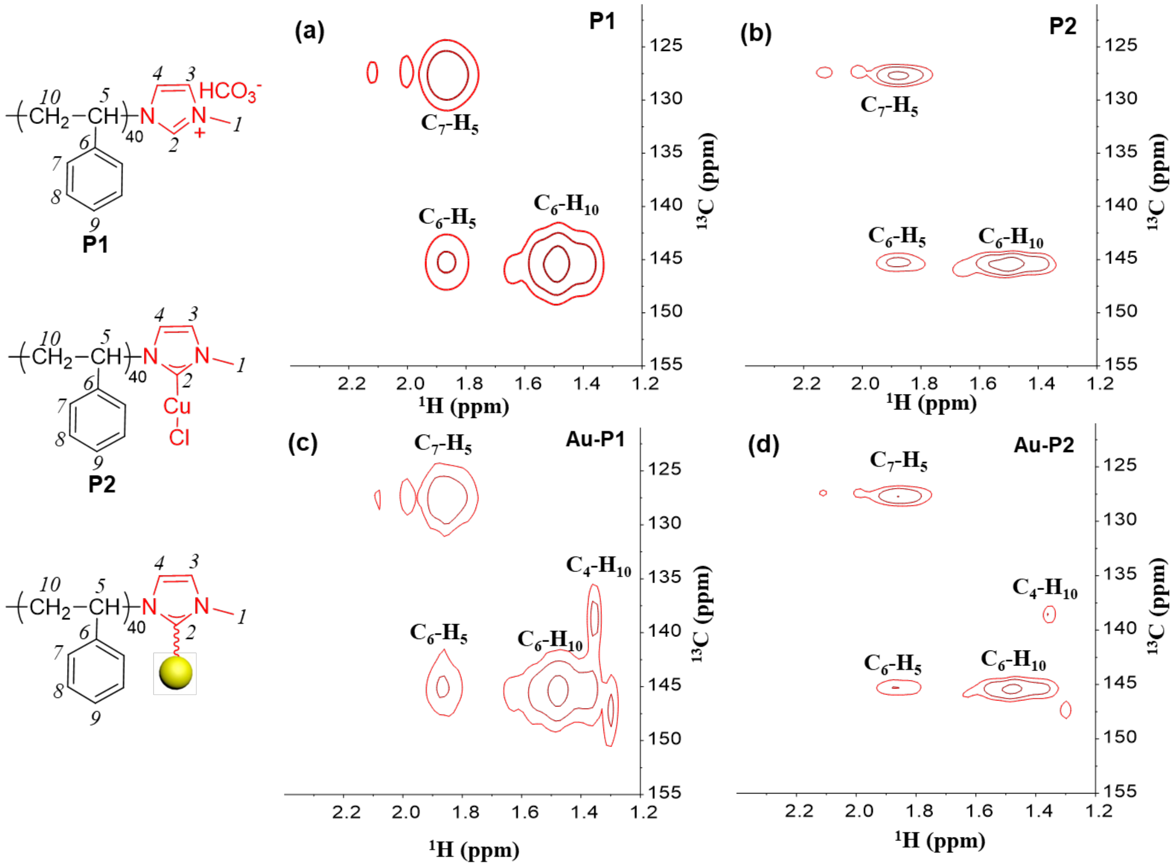


Figure S5. Partially enlarged 2D HMBC spectra of (a) P1, (b) P2, (c) Au-P1 and (d) Au-P2.

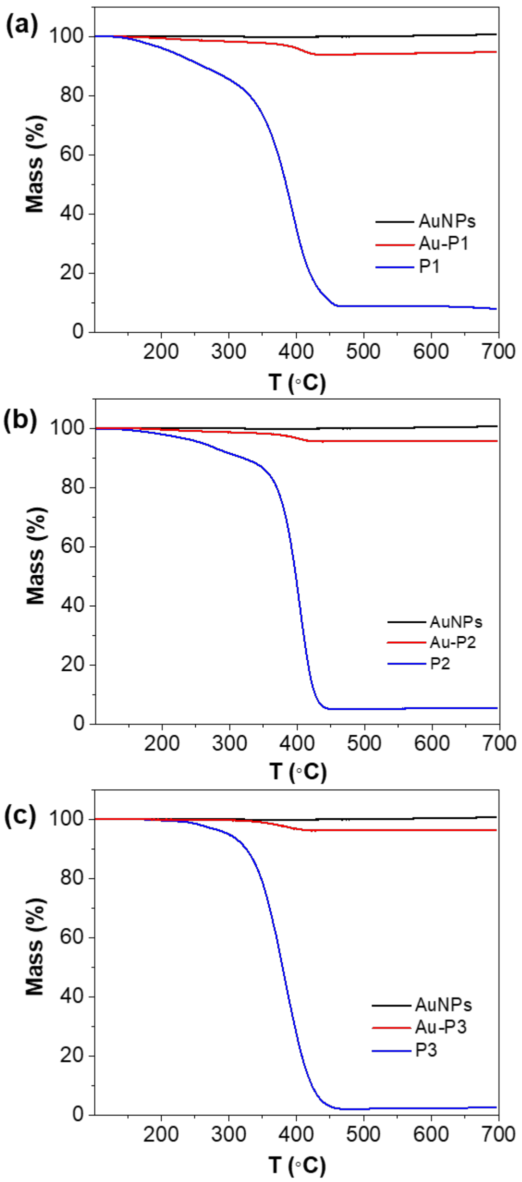


Figure S6. TGA thermograms of (a) AuNPs, Au-P1, P1, (b) AuNPs, Au-P2, P2 and (c) AuNPs, Au-P3, P3.

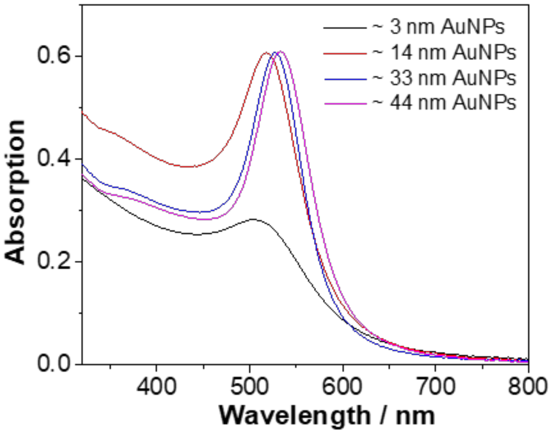


Figure S7. UV-vis spectra of different size of AuNPs capped with CA.

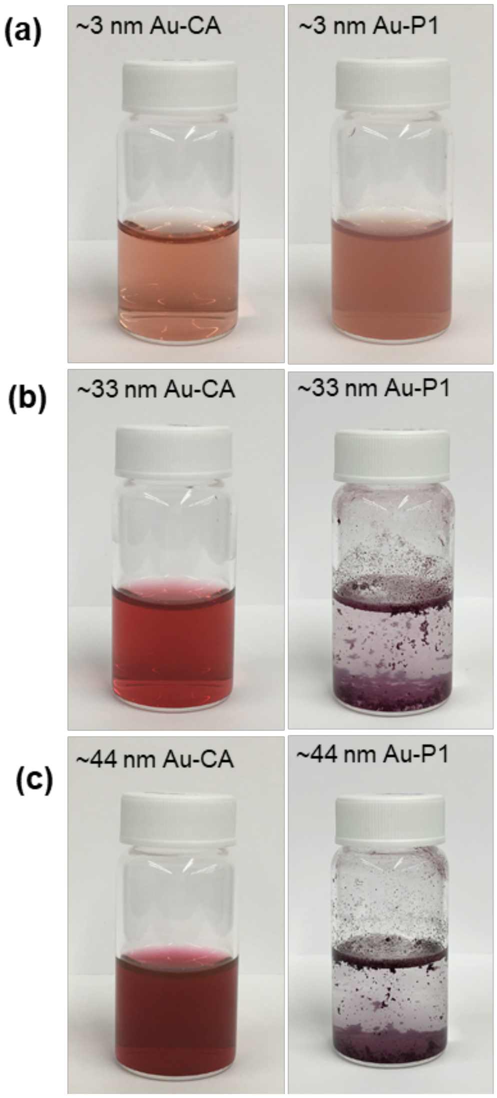


Figure S8. The digital images of Au-CA with different sizes before and after modification with P1.

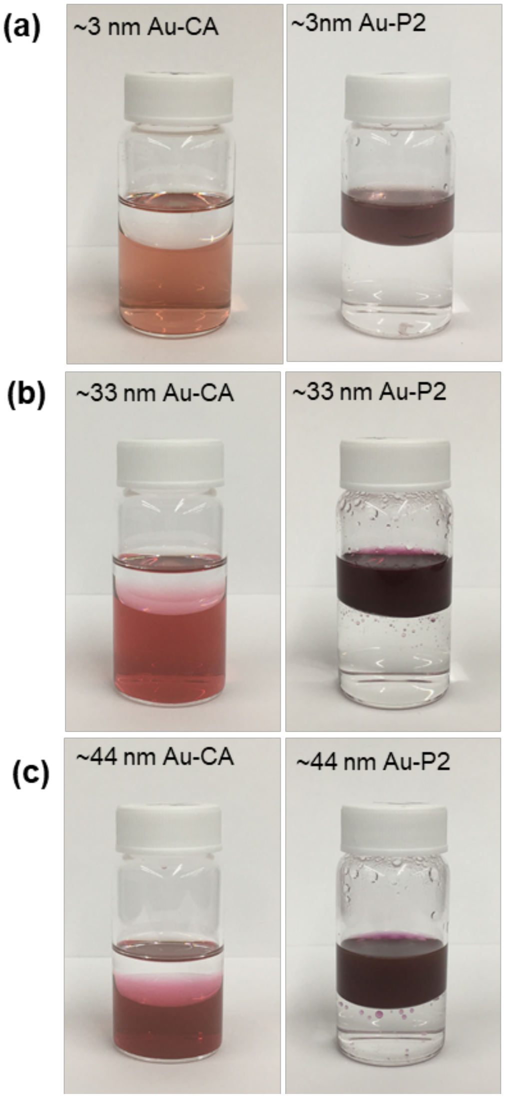


Figure S9. The digital images of Au-CA with different sizes before and after modification with P2.

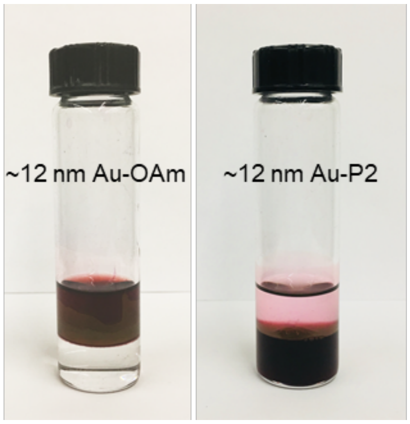


Figure S10. The digital images of Au-OAm before and after modification with P2.

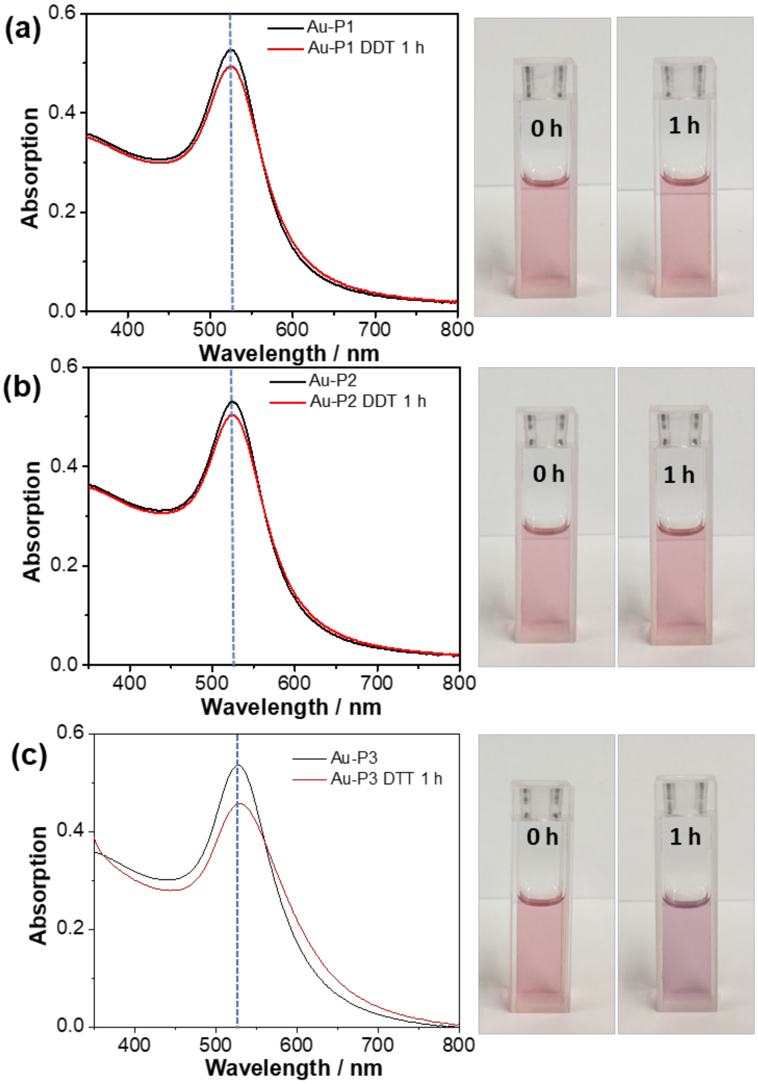


Figure S11. The stability of (a) Au-P1, (b) Au-P2 and (c) Au-P3 at 1.5 M of DDT and corresponding digital images before and after chemical treatment.

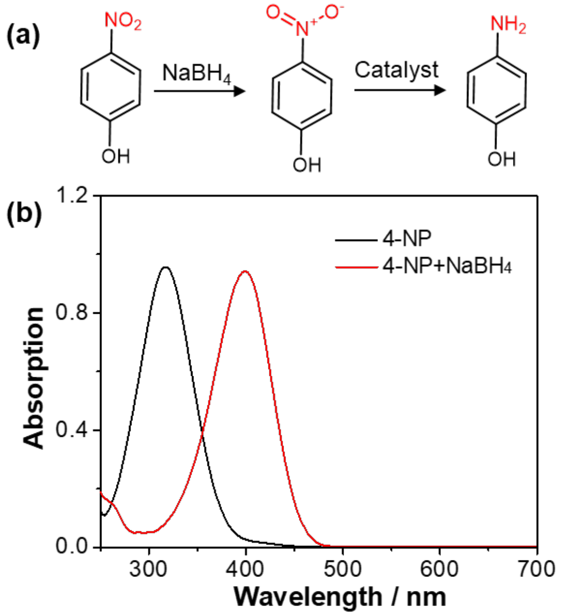


Figure S12. (a) Reduction of 4-nitrophenol. (b) UV-vis spectra of 4-nitrophenol and mixture of 4-nitrophenol and $NaBH_4$.

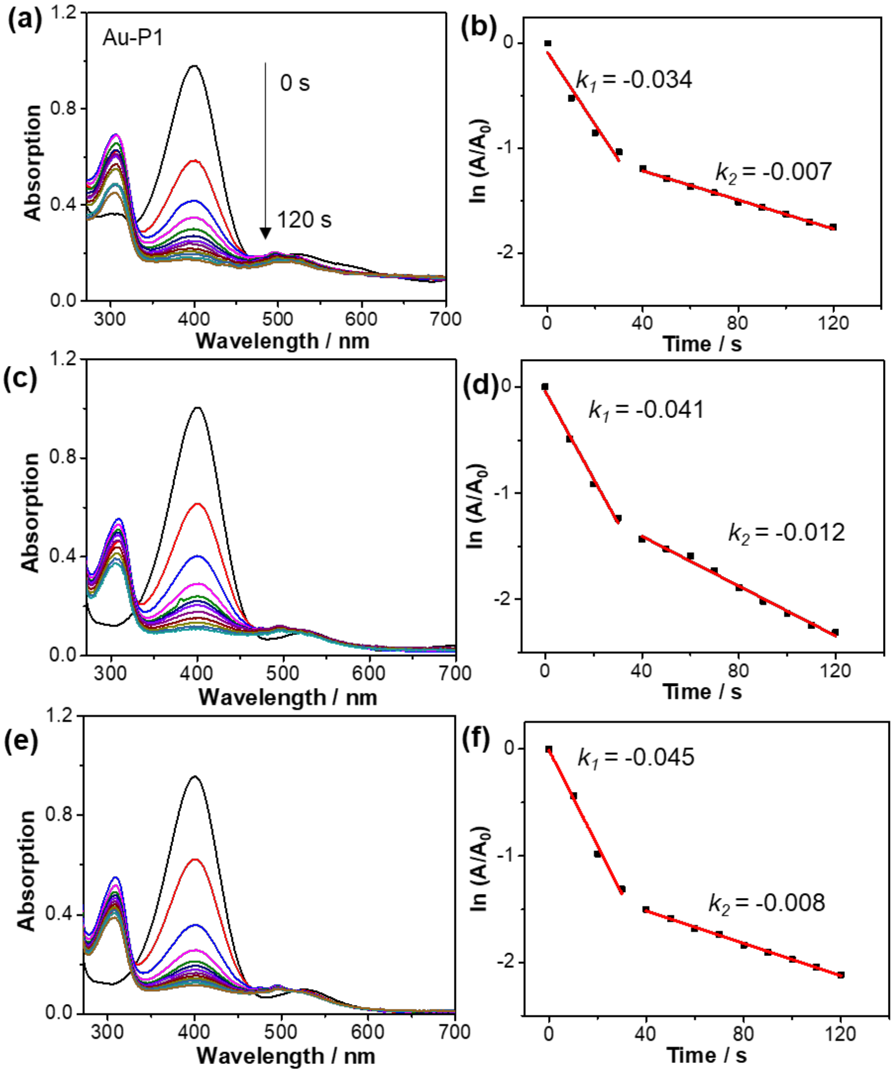


Figure S13. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Au-P1 as catalyst. The spectra were recorded every 10 s.

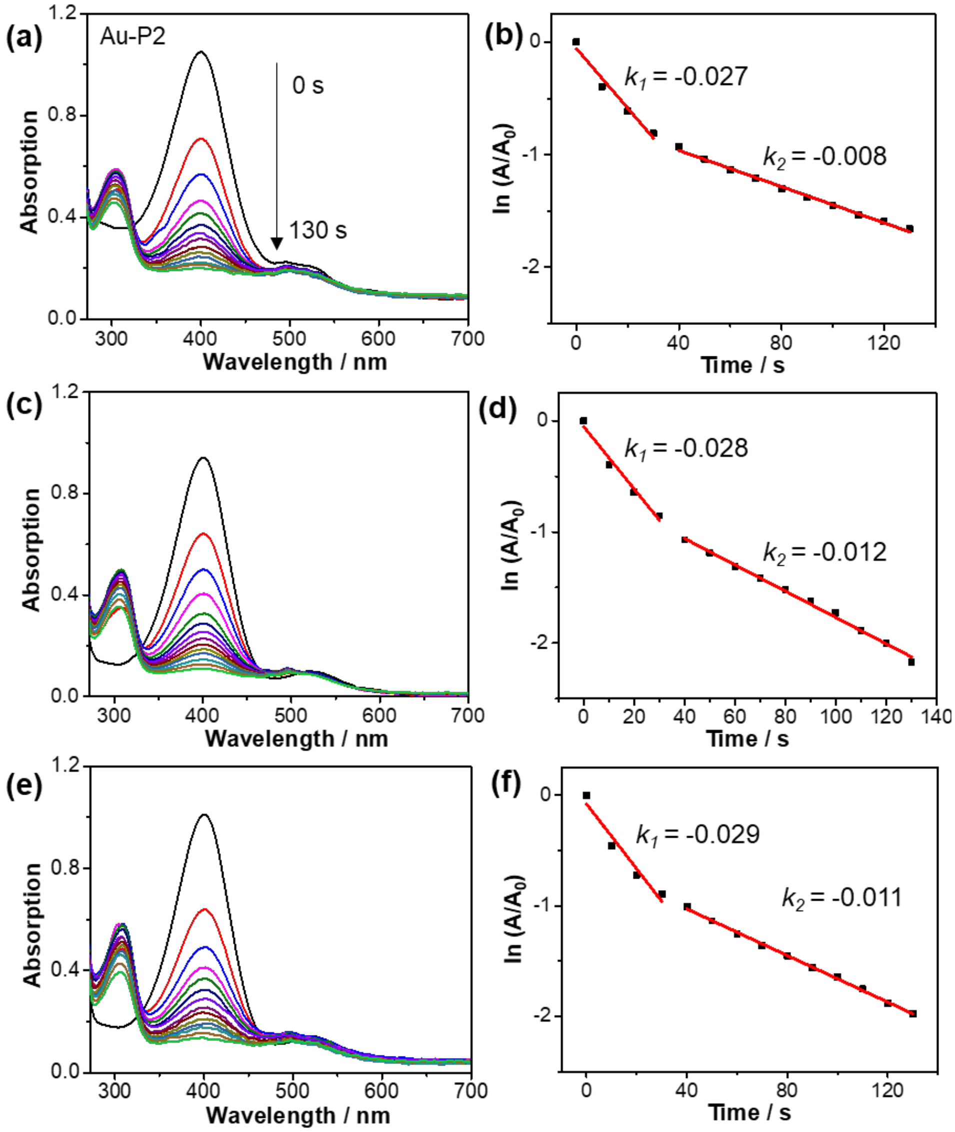


Figure S14. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Au-P2 as catalyst. The spectra were recorded every 10 s.

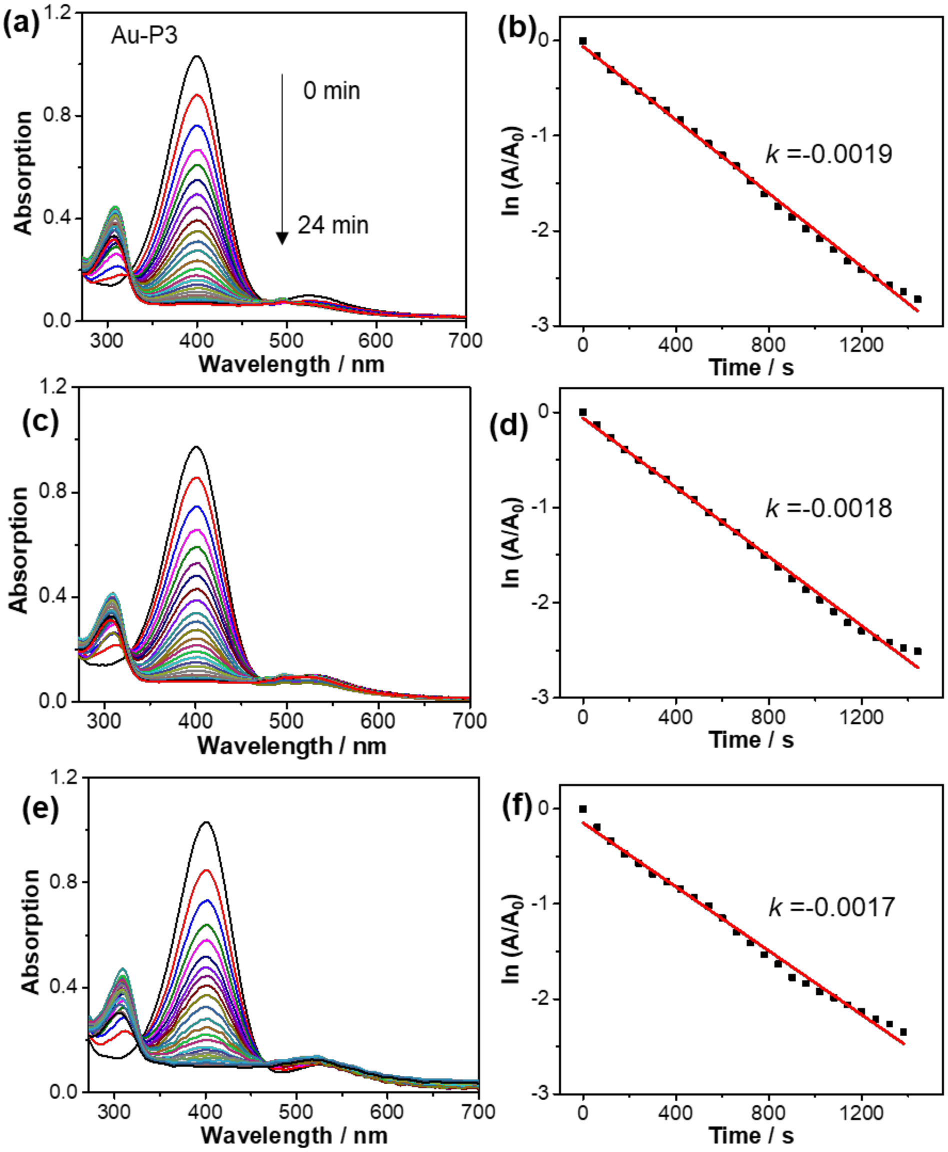


Figure S15. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A_0) *versus* time for the reduction of 4-nitrophenol using Au-P3 as catalyst. The spectra were recorded every 1 min.

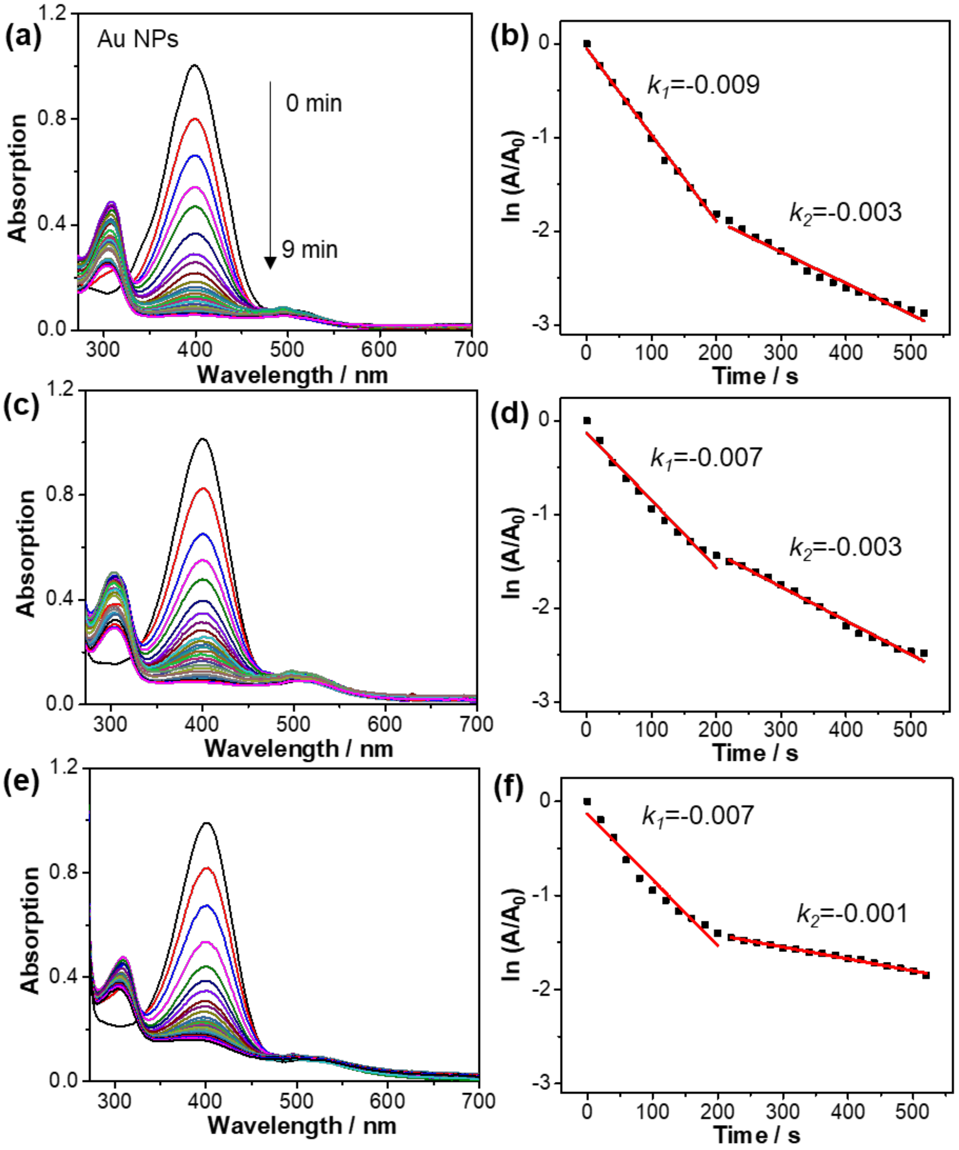


Figure S16. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Au-CA as catalyst. The spectra were recorded every 20 s.

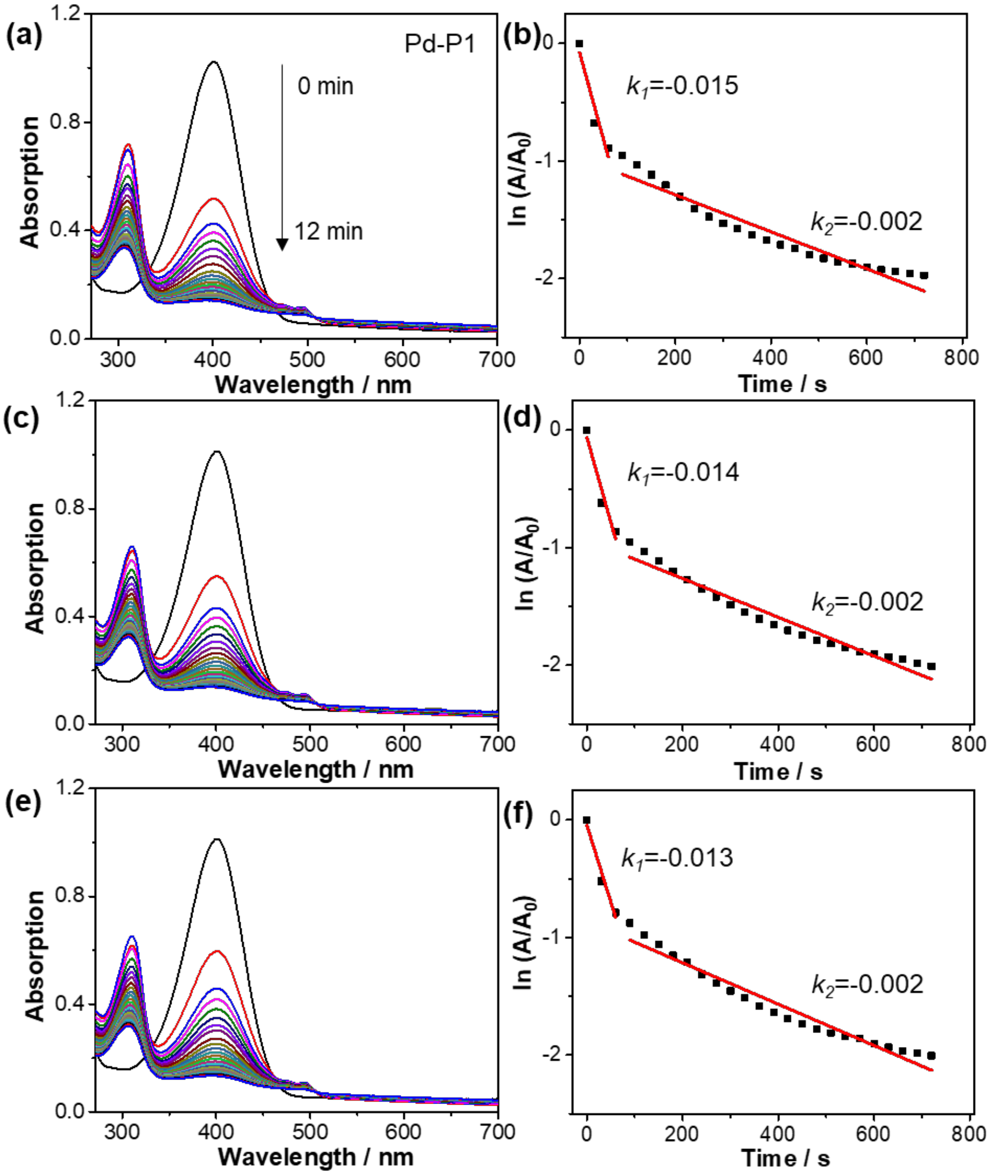


Figure S17. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Pd-P1 as catalyst. The spectra were recorded every 30 s.

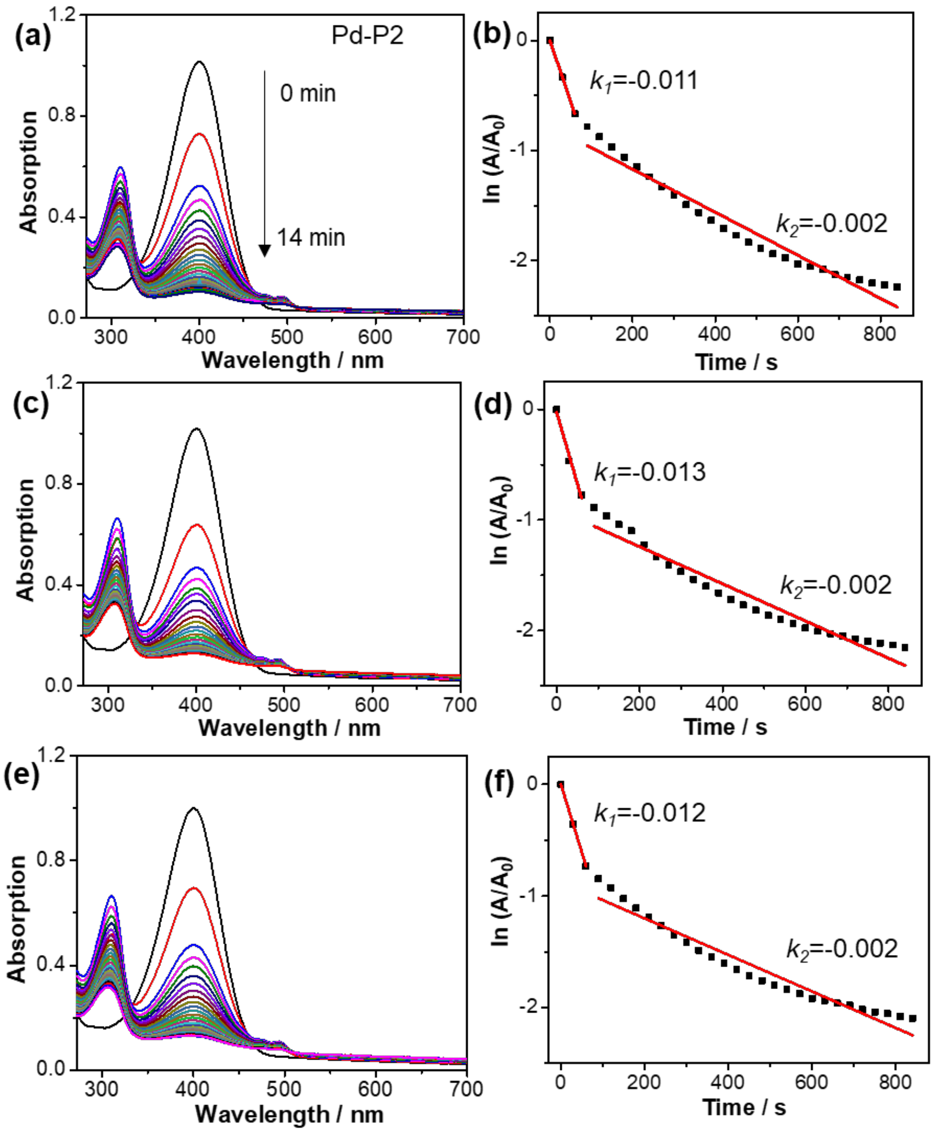


Figure S18. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Pd-P2 as catalyst. The spectra were recorded every 30 s.

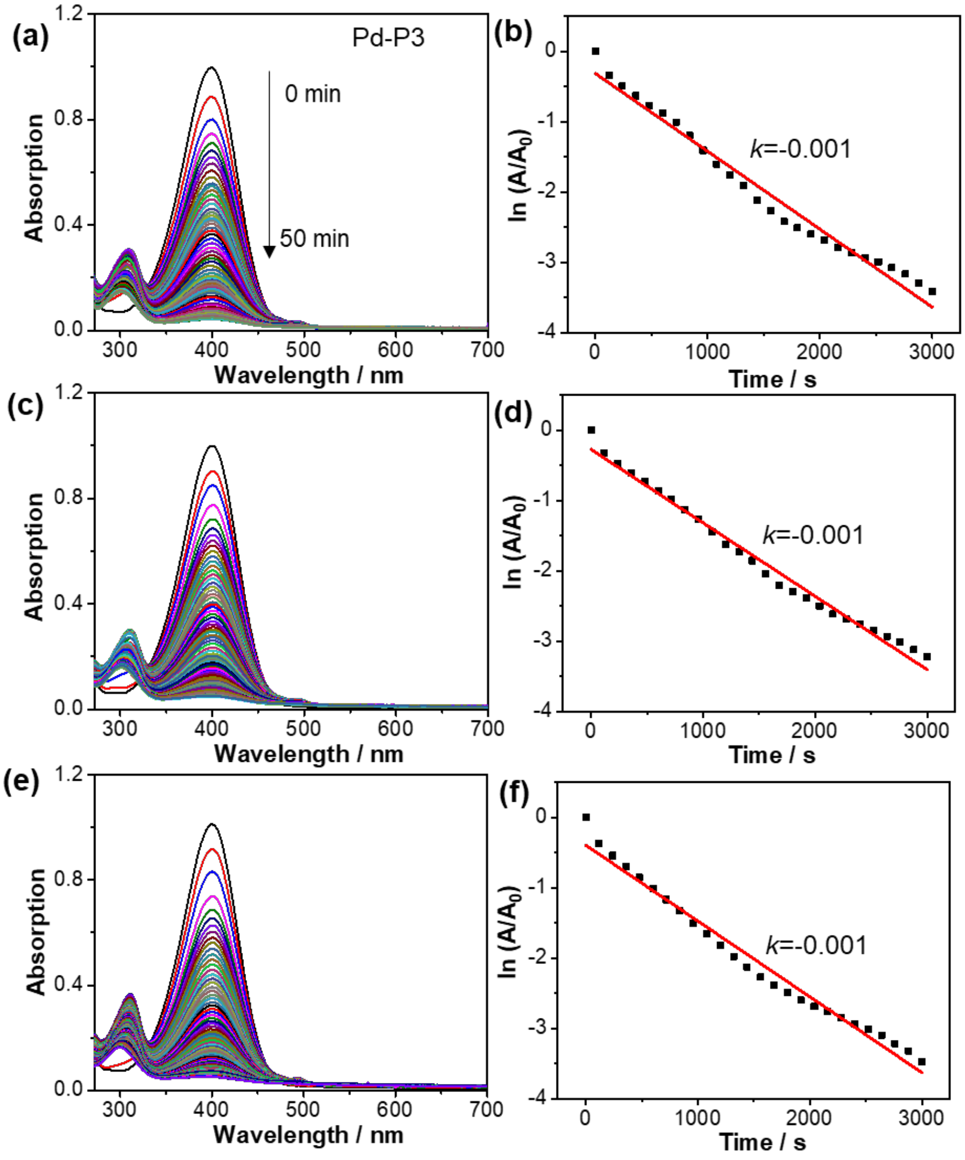


Figure S19. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Pd-P3 as catalyst. The spectra were recorded every 30 s.

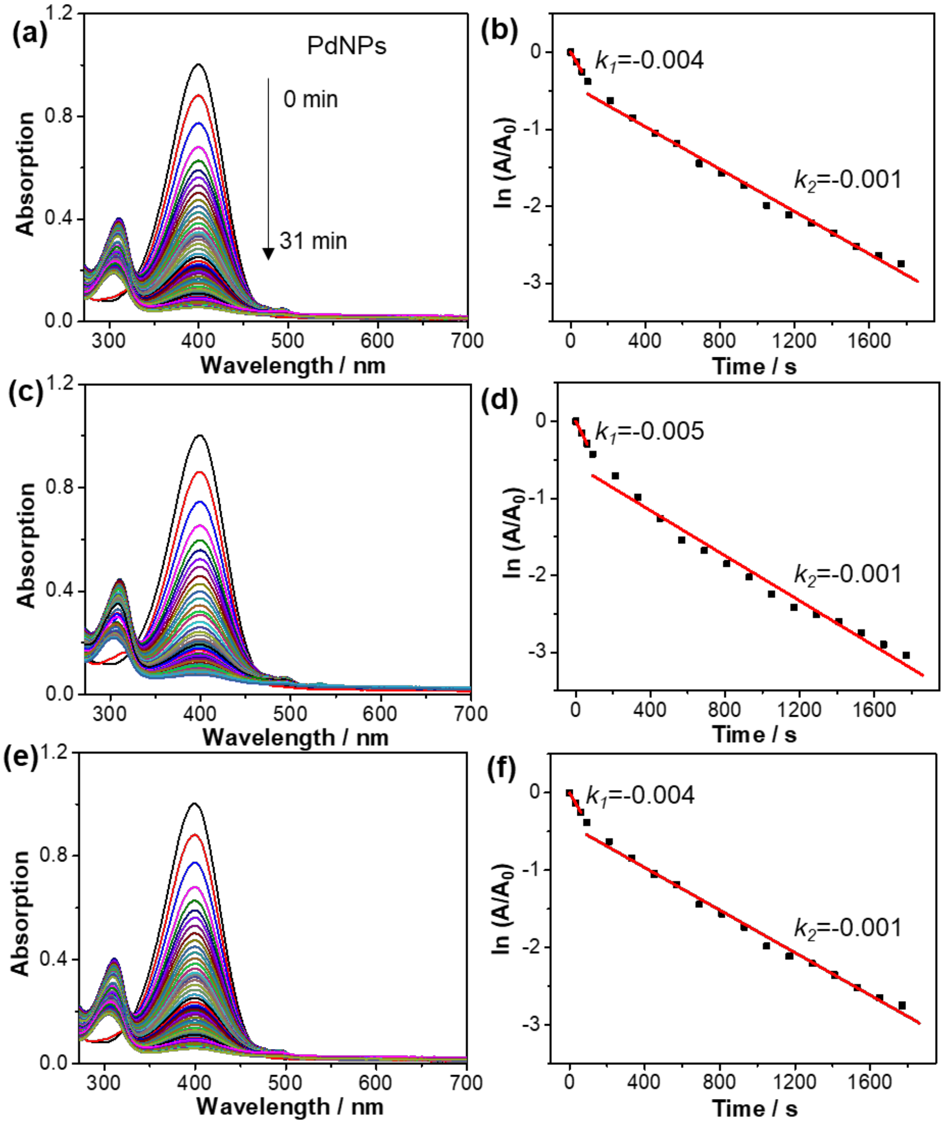


Figure S20. (a, c, e) Three repeated UV-vis spectra and (b, d, f) corresponding plots of ln(A/A$_0$) *versus* time for the reduction of 4-nitrophenol using Pd-CA as catalyst. The spectra were recorded every 30 s.

Supporting References

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