Electronic Supplementary Information

Gold Nanoparticles as Electron Reservoir Redox Catalysts for the Reduction of 4-Nitrophenol: Strong Stereoelectronic Ligand Influence

Roberto Ciganda, Na Li, Christophe Deraedt, Sylvain Gatard, Pengxiang Zhao, Lionel Salmon, Ricardo Hernández, Jaime Ruiz, Didier Astruc*

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1.- General data

All the solvents and chemicals were used as received.

- The **UV-vis.** absorption spectra were measured with a Pekin-Elmer Lambda 19 UV-vis. spectrometer.

- **Dynamic Light Scattering (DLS)** measurements were made using a Malvern Zetasizer 3000 HSA instrument at 258K at an angle of 90°.

- **Transmission Electron Microscopy (TEM) images** were recorded by Dr. Lionel Salmon at the “Laboratoire de Chimie de Coordination” (LCC), CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France.

- **$^1$H NMR** spectra were recorded at 25°C with a Bruker AC 200 MHz spectrometer. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me₄Si (TMS).
2.- AuNPs synthesis and characterizations

- AuNPs 1, 2, 3 and 4

The AuNPs 1-4 were synthesized following reported procedures.\textsuperscript{a,b} In brief, generally, tetrachloroaurate acid (8.5 mg, 0.025 mmol) and the triazole ligand (0.125 mmol for 1, 2 and 0.05 mmol for 3, 4) were dissolved in deionized water (10 mL), and the obtained solution was stirred for 10 min. Then, a freshly prepared sodium borohydride (0.1 mmol) aqueous solution (1 mL) was dropwise added under vigorous stirring in a period of 5 min. After further stirring for 30 min, the AuNPs were purified by dialysis for 24 h to remove the excess ligands and salts. The triazole-AuNPs were kept in aqueous solution at 22 °C.

\textbf{Fig. S1.} a) UV-vis. spectrum (SPB at 504 nm), and b) DLS size-distribution histogram (d = 141 nm, in aqueous solution) of AuNPs 2.

\textbf{Fig. S2.} TEM image of AuNPs 2 (d = 3 nm).
Fig. S3. TEM of AuNPs 3 (a); size distribution of 3 (b).

- **AuNPs 5**

AuNPs 5 were synthesized according to a reported procedure. Briefly, HAuCl$_4$·3H$_2$O (0.009 mmol, 3.5 mg) and DEND550 (0.001 mmol, 6.5 mg) were dissolved in 5 mL Milli-Q water. After being stirred for 10 minutes, 1 mL of freshly prepared NaBH$_4$ (0.045 mmol, 1.7 mg) water solution was added dropwise into the solution with vigorous stirring. The Au-DEND550-1 solution that was obtained was further stirred for 30 minutes and was dialyzed against a large volume of water (2 × 4 h).

Fig. S4. TEM image (d = 3.5 nm) and DLS of AuNPs 5 (d = 220 nm).
- **AuNPs 6**

1.62 × 10^{-2} mmol of polymer trz-PEG (dimer Mw = 514 g.mol^{-1}, 0.8368 mg) is dissolved in 0.3 mL of water in a Schlenk flask, and an yellow solution of HAuCl_{4} (3.2 × 10^{-3} mmol in 0.11 mL water) is added to the solution of the polymer. 2.8 mL of water is added, and the solution is stirred for 5 min at 20°C. A 0.1 mL aqueous solution containing 3.2 × 10^{-2} mmol of NaBH_{4} is added dropwise, provoking the appearance of a red color corresponding to the reduction of Au^{III} to Au^{0} and AuNP formation.

![UV-vis spectrum of AuNPs 6](image)

**Fig. S5.** UV-vis. spectrum of AuNPs 6: a plasmon band is observed at 519 nm.
30 mL of MeOH (HPLC grade) and 5.0 mL of acetic acid were mixed in a 150 mL Erlenmeyer flask by stirring for 2-5 min. Then, 78.0 mg (0.2 mmol) of tetrachloroauric acid (HAuCl₄·xH₂O) (99.99%) and 58 mg (0.1 mmol) of SH-PEG₅₅₀CH₃ were added to the above mixed solvents and dissolved by stirring for 5 min, which gave a clear, yellow solution. Then, 75.0 mg (2.0 mmol) of sodium borohydride (NaBH₄, 99%) was dissolved in 5.0 mL of Nanopure water. The NaBH₄ solution was dropwise added into the above solution with rapid stirring. With the first drop of NaBH₄ that was added, the HAuCl₄ solution immediately turned from yellow to dark brown. Rapid stirring was continued for 2 h. The reaction was kept overnight with slower stirring. The solvents were removed in vacuo. CH₂Cl₂ (100 mL) was added to the waxy nanoparticles. The organic solution was dark brown and was washed twice with salted water. After drying with Na₂SO₄, and filtration, the solvent was removed in vacuo, and the solid was dissolved in 100mL ultra pure water. The nanoparticles were further purified by dialysis in pure water over a 7-days period, (water was changed twice daily).
**Fig. S7.** $^1$H NMR spectrum of AuNPs 7 in D$_2$O.

**Fig. S8.** UV-vis. spectrum of AuNPs 7 in H$_2$O. Abs$_{max}$: 520 nm
Fig. S9. TEM images of AuNPs 7 with an average core size of 3.5 nm.

- **AuNPs 8**

The large Au-thiolate-PEG$_{550}$ nanoparticles 8 were obtained from the citrate gold nanoparticles 9 by exchange of citrate ligands with SH-PEG$_{550}$CH$_3$ to yield the corresponding thiolate-AuNPs. This reaction was performed according the literature. A large excess of thiol ligand was used: 100 monolayers/ particle, estimated by assuming that the occupied surface area by a single thiol molecule is ca. 0.20 nm$^2$. Using this calculation, 10 mg of ligand 1 was added into the citrate AuNP solution. The mixture was rapidly stirred at room temperature for 20 h during which the color of the solution became slightly darker. The nanoparticles were further purified by dialysis in pure water over a 7-days period. The plasmon band of these particles was observed at 524 nm. The size of the gold core of the AuNPs that was measured from TEM images was 13.5 nm +/- 1 nm.
**Fig. S10.** UV-vis. spectrum of AuNPs 8 in H$_2$O $\lambda_{\text{max}}$: 524 nm.

**Fig. S11.** TEM images of AuNPs 8 with an average core size of \( \approx 13.5 \)nm.
Concentrated citrate stabilized AuNPs 9 (≈1 mM) were synthesized using a modified Frens method. In a 500 mL two-neck round-bottom flask equipped with a condenser and a stir bar, 250 mL of 1.056 mM aqueous solution of HAuCl₄ was brought to boil while stirring vigorously. 11 mL of 5% aqueous solution of trisodium citrate (n_{citrate}/n_{Au} = 7) was quickly added to the gold chloride solution, resulting in a series of color changes from pale yellow to colorless, then dark gray, purple, red, and finally dark wine red. The color change occurred within a period of 5 min, and the solution was subsequently refluxed for an additional 15 min, removed from the oil bath, and cooled down to room temperature. The plasmon band of these AuNPs was observed at 520 nm. The average diameter of the AuNPs as determined by TEM measurement was 13.5 nm.

**Fig. S12.** UV-vis. spectrum of AuNPs 9 in H₂O: λ_{max}: 520 nm (a); TEM images of AuNPs 9 with an average core size of ≈ 13.5 nm (b).
3.- UV-vis spectra, $k_{\text{app}}$ and $E_a$ for the catalytic reactions of the AuNPs

General procedure for the reduction of 4-NP

4-NP (1 equiv.) was mixed with NaBH$_4$ (81 equiv.) in water in air. Then the solution containing AuNPs (0.2 mol%) was added. The color of the solution changed from light yellow to dark yellow due to the formation of 4-nitrophenolate ion. Then, this solution lost its dark yellow color with the time after addition of AuNPs. The reaction was monitored by UV-vis. spectroscopy. All the reactions were conducted at 20°C, except for the AuNPs 1 and AuNP 2 (13°C).

UV-vis spectra, $k_{\text{app}}$ and $E_a$ for the catalytic reactions of the AuNPs

- AuNPs 1

![UV-vis spectra](image-url)
Fig. S13. Reduction of 4-NP by AuNPs 1 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( C_t/C_0 \right)$ ($C_t$ = concentration of 4-NP at time $t$, $C_0$ = concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs 1/T (in K) (c) )

$k_{app} = 1.2 \times 10^{-2}$

$y = -2936.2x + 5.8203$
The Arrhenius equation gives an estimate of the activation energy \((E_a)\) of the systems.

This equation is given in the form:

\[ k_{\text{app}} = Ae^{\frac{E_a}{RT}} \]

The former form can be written equivalently as:

\[ \ln k_{\text{app}} = \ln A - \frac{E_a}{RT} \]

where:
- \(k_{\text{app}}\) = rate constant
- \(A\) = pre-exponential factor
- \(E_a\) = activation energy (KJ mol\(^{-1}\))
- \(R\) = gas constant (8.31446 JK\(^{-1}\)mol\(^{-1}\))
- \(T\) = temperature (K)

When plotted in the manner described above, the slope of the line is equal to \(-E_a/R\).

- **AuNPs 2**

(a)
Fig. S14. Reduction of 4-NP by AuNPs 2 (UV-vis spectra of the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left(\frac{C_t}{C_0}\right)$ ($C_t = $ concentration of 4-NP at time $t$, $C_0 =$ concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs $1/T$ (in K) (c).

For the AuNPs 1 and 2, the temperatures that are chosen are 3ºC, 7ºC and 13ºC.
- **AuNPs 3**

(a) Absorbance vs. Wavelength (nm)

(b) 

\[ \ln \left( \frac{C_t}{C_0} \right) = k_{\text{app}} \times t \]

\[ k_{\text{app}} = 1.4 \times 10^{-2} \]
**Fig. S15.** Reduction of 4-NP by AuNPs 3 (UV-vis spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of \(-\ln (C_t/C_0)\) (\(C_t\) = concentration of 4-NP at time \(t\), \(C_0\) = concentration of 4-NP at \(t = 0\)) as a function of the time (in seconds) (b) and the plots of \(\ln k_{app}\) vs \(1/T\) (in K) (c) )
- AuNPs 4

(a) Absorbance

(b) $k_{\text{app}} = 6.7 \times 10^{-3}$
Fig. S16. Reduction of 4-NP by AuNPs 4 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln (C_t/C_0)$ ($C_t$ = concentration of 4-NP at time $t$, $C_0$ = concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of \(\ln k_{\text{app}}\) vs $1/T$ (in K) (c) )

For the AuNPs 3 and 4, the temperatures that are chosen are 10°C, 20°C, 25°C and 30°C.
Fig. S17. Reduction of 4-NP by AuNPs 5 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( \frac{C_t}{C_0} \right)$ ($C_t =$ concentration of 4-NP at time $t$, $C_0 =$ concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs 1/T (in K) (c) )
The UV-vis. spectra show absorbances that are larger than 2. Thus, with respect to the Beer-Lambert law, it was considered that these results were not relevant, and therefore they were not used to build up the kinetics plots.

- **AuNPs 6**

![Graph](image)

(a) Absorbance vs. Wavelength (nm)

(b) 

\[ k_{app} = 1.1 \times 10^{-2} \]
Fig. S18. Reduction of 4-NP by AuNPs 6 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( \frac{C_t}{C_0} \right)$ ($C_t = $ concentration of 4-NP at time $t$, $C_0 = $ concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs $1/T$ (in K) (c)).
Fig. S19. Reduction of 4-NP by AuNPs 7 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( C_t/C_0 \right)$ ($C_t$ = concentration of 4-NP at time $t$, $C_0$ = concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{\text{app}}$ vs $1/T$ (in K) (c).

For the AuNPs 7, the temperatures that are chosen are 20°C, 35°C and 40°C.
**AuNPs 8**

**Fig. S20.** Reduction of 4-NP by AuNPs 8 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( C_t/C_0 \right)$ ($C_t =$ concentration of 4-NP at time $t$, $C_0 =$ concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs. $1/T$ (in K) (c).
- AuNPs 9

**Fig. S21.** Reduction of 4-NP by AuNPs 9 (UV-vis. spectra for the reduction of 4-NP by AuNPs (a), the corresponding plots of $-\ln \left( \frac{C_t}{C_0} \right)$ ($C_t =$ concentration of 4-NP at time $t$, $C_0 =$ concentration of 4-NP at $t = 0$) as a function of the time (in seconds) (b) and the plots of $\ln k_{app}$ vs $1/T$ (in K) (c) )
4. UV-vis. spectra for the various solutions in Figure 2

The addition of NaBH$_4$ to the trz-AuNPs (3) leads to color change and to a blue shift of the surface plasmon band (SPB).

**Fig. S22.** UV-vis. spectra of the different solution for trz-AuNPs (3) with various amounts of NaBH$_4$
5.- References


