Electronic Supplementary Information

Synthesis and Solution Isomerization of Water-Soluble Au₉ Nanoclusters Prepared by Nuclearity Conversion of [Au₁₁(PPh₃)₈Cl₂]Cl

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Contents
Syntheses ........................................................................................................................... 1
NMR .................................................................................................................................... 2
ESI-MS Spectra .................................................................................................................. 8
UV-VIS Spectra .................................................................................................................. 9
Proposed crystal structures of water-soluble [Au₉(L)₉]³⁺ ................................................................... 12
Cytotoxicity of AuNCs against 3T3 cells ............................................................................... 13
Cytotoxicity of AuNCs against A549 cells ............................................................................ 15
References ......................................................................................................................... 16

SYNTHESSES

Synthesis of triphenylphosphine monosulfonate (TPPMS)

![Scheme S1. Synthesis of triphenylphosphine monosulfonate (TPPMS).](image)

Synthesis of TPPMS followed a reported procedure.¹ Fuming sulfuric acid (6 mL, 18-24% SO₃) was placed in a 100-mL, three-necked flask charged with a 60-mL dropping funnel, and cooled in an ice bath to 0 °C. The ice bath as well as the reaction were stirred, and triphenylphosphate (PPh₃) (2.0 g, 7.6 mmol) was added rapidly. The reaction mixture was kept at 0 °C until PPh₃ had completely dissolved (2 hours). The mixture was then stirred at room temperature for 18 h. Afterwards, the reaction mixture was cooled again to 0 °C, and cold water (30 mL) was added dropwise with vigorous stirring. NaOH (7.5 M, ~25 mL) was used to bring the pH to 8. A white foam-like solid was observed during neutralization process. The product was filtered with little suction then transferred to a flask, and water (50 mL) was added. The recrystallization setup was then placed in the 4°C fridge. A white solid was observed at the bottom of the flask. The product was filtered and transferred to a flask with n-pentane (20 mL) and sonicated for 15 minutes to remove PPh₃. This process was repeated 3 times. The pentane was discarded and the white solid freeze dried to give the product as a white solid (2.0 g, 78%).¹³H NMR (400 MHz, D₂O): δ 7.69 (d, J = 7.16 Hz, 1H), 7.64 (d, J = 7.55 Hz, 1H), 7.17 (m, 12H).³¹P NMR (162 MHz, D₂O): δ = 5.63 (s).

Synthesis of triphenylphosphine gold (I) chloride (Au(PPh₃)Cl)

![Scheme S2. Synthesis of Au(PPh₃)Cl.](image)

Synthesis of Au(PPh₃)Cl followed a literature protocol.² Argon was bubbled into 95% ethanol for 15 min prior to use. Hydrogen tetrachloraurate trihydrate (HAuCl₄·3H₂O, 0.64 g, 1.6 mmol) was placed in a two-necked 100-mL flask which was then evacuated and backfilled twice with argon. Ethanol (10 mL) was added to the flask and stirred, forming a yellow solution. To this solution, PPh₃ (0.86 g, 3.3 mmol) in ethanol (30 mL) was added. The mixture was colorless briefly, before a white precipitate appeared. The reaction was then stirred for 2 minutes. The product was removed by filtering through a medium porosity glass frit, washed with diethyl ether (15 mL×3), and then dried in vacuo. The solid on the frit was dissolved with DCM, which was then concentrated

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¹ Fuming sulfuric acid
² Literature protocol
to ~5 mL and then precipitated slowly on ice by pentane (added at 5 mL/hr for 4 mL). The product formed was filtered and dried in a vacuum oven. The supernatant of precipitation was repurified in the similar manner. The purified product showed a single spot on TLC (1:3 hexanes/DCM, Rf ~ 0.5). The final product was obtained as a white solid (0.71 g, 89%). ^1H NMR (400 MHz, CDCl₃): δ 7.46 – 7.55 (m, 15H). ^31P NMR (162 MHz, CDCl₃): δ 33.77.

**NMR SPECTRA**

![Figure S1](image1.png)  
**Figure S1.** ^31P NMR spectrum of TPPMS in D₂O. A very small amount (<1%) of the oxide (36.44 ppm) is observed in the recrystallized TPPMS.

![Figure S2](image2.png)  
**Figure S2.** ^31P NMR spectrum of Au(PPh₃)Cl in CDCl₃.
Figure S3. $^1$H NMR spectrum of $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\text{Cl}$ in CDCl$_3$.

Figure S4 $^{31}$P NMR spectrum of $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\text{Cl}$ in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 0.6 mM of [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O.

Figure S6. $^{31}$P NMR spectrum of [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O.

Figure S7. $^1$H NMR spectrum of 0.6 mM of [Au$_9$(DPPBA)$_8$]Cl$_3$ in D$_2$O with 20 mM NaOH.
Figure S8. $^{31}$P NMR spectrum of [Au$_9$(DPPBA)$_8$]Cl$_3$ in D$_2$O with 20 mM NaOH.

Figure S9. 2D DOSY NMR spectrum of TPPMS in D$_2$O at 289.15 K. Chemical shifts (ppm) are shown on the x-axis and the diffusion coefficients ($10^{-9}$ m$^2$ s$^{-1}$) on the y-axis of the DOSY plot.

Figure S10. 2D DOSY NMR spectrum of DPPBA in D$_2$O with 20 mM NaOH at 289.15 K. Chemical shifts (ppm) are shown on the x-axis and the diffusion coefficients ($10^{-9}$ m$^2$ s$^{-1}$) on the y-axis of the DOSY plot.
Figure S11. $^1$H NMR spectra of (A) PPh$_3$ and (B) [Au$_{11}$PPh$_3$)$_8$Cl$_2$]Cl in CDCl$_3$.

Figure S12. $^1$H NMR spectra of (A) TPPMS, and (B) [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O. Peak assignments are aided by the 2D COSY spectrum (Fig. S14).
**Figure S13.** $^1$H NMR spectra of (A) DPPBA and (B) [Au$_9$(DPPBA)$_8$]Cl$_3$ in D$_2$O with 20 mM NaOH. Peak assignments are aided by the 2D COSY spectrum (Fig. S15).

**Figure S14.** $^1$H-$^1$H correlation spectra (COSY) of [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O.
**Figure S15** $^1$H–$^1$H correlation spectra (COSY) of [Au$_9$(DPPBA)$_8$]$^{3+}$ in D$_2$O with 20 mM of NaOH.

**ESI-MS SPECTRA**

**Figure S16.** Experimental and simulated isotope peak pattern overlays of 1528.33 $m/z = [\text{Au}_9(\text{TPPMS})_8]^{3+}$-SO$_3$Na.

**(A)**

**Figure S17.** Experimental and simulated isotope peak pattern overlays of (A) 1053.81 $m/z = [\text{Au}_9(\text{DPPBA})_8 - 7\text{H}]^{3+}$, (B) 1539.04 $m/z = [[\text{Au}_9(\text{DPPBA})_3]^{2-} + 2\text{H} + \text{CH}_3\text{O}]^{-}$ and (C) 2108.70 $m/z = [\text{Au}_9(\text{DPPBA})_8 - 5\text{H}]^{2-}$.
UV-VIS SPECTRA

**Figure S18.** UV-Vis spectrum of $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\text{Cl}$ in DCM.

**Figure S19.** UV-Vis spectrum of $[\text{Au}_9(\text{TPPMS})_8]\text{Cl}_3$ in water (0.125 mg/mL).

**Figure S20.** UV-Vis spectrum of $[\text{Au}_9(\text{DPPBA})_8]\text{Cl}_3$ in 20 mM NaOH (0.5 mg/mL).
Figure S21. UV-Vis spectra of [Au₉(DPPBA)₈]Cl₃ (0.25 mg/mL) in pH 3 water (dashed line), and in pH 3 MeOH/water (1:1) (solid line).

Figure S22. UV-Vis spectra of [Au₉(DPPBA)₈]Cl₃ (0.25 mg/mL) in pH 5.5 water (dashed line) and in pH 5.5 MeOH/water (1:1) (solid line).

Figure S23. UV-Vis spectra of [Au₉(DPPBA)₈]Cl₃ (0.25 mg/mL) in pH 12 water (dashed line) and in pH 12 MeOH/water (1:1) (solid line).
Figure S24. Absorption spectra of [Au₉(DPPBA)₈]Cl₅ in EtOH (20 mM NaOH), immediately after heating to 60 °C (red line) and after cooling to 15 °C (black line). The spectra were smoothed using an FFT filter function in OriginPRO to reduce noise.

Figure S25. Raw Vis-NIR absorption spectra of Au₉(DPPBA)₈Cl₅ in ethanol. An artifact present at 535 nm arises from the light source.

Figure S26. Au₉(TPPMS)₈Cl₅ in conc. HCl (86%, 9 M). No color change was detected. The suspension turned into a completely clear solution after 2 days.
PROPOSED STRUCTURES OF WATER-SOLUBLE [AU₉(L)₈]³⁺

**Figure S27.** Proposed C₄ ‘crown’ isomer structure of Au₉(TPPMS)₈Cl₃. The structure shows Au in yellow, P in orange, S in greenish yellow, O in red and C in grey. H atoms are omitted for clarity. Structures were obtained by replacing P(C₆H₄OMe-p)₃ ligands in the C₄ isomer in Ref. 3 (cf Fig. 1A) with TPPMS and minimizing the energy using the Universal force field algorithm (UFF) in Avogadro software.

(A)  
(B)

**Figure S28.** Proposed structure of Au₉(DPPBA)₈Cl₃ as (A) the C₄ (crown) isomer and (B) the D₂h (butterfly) isomer. The structures show Au in yellow, P in orange, O in red and C in grey. H atoms are omitted for clarity. Structures were obtained by replacing P(C₆H₄OMe-p)₃ ligands with DPPBA in the C₄ and D₂h crystal structures in Ref. 3 (cf Fig. 1), and minimizing the energy using the universal force field algorithm (UFF) in the Avogadro software.
CYTOTOXICITY OF AuNCs AGAINST 3T3 CELLS.

Dose response curves were fitted using OriginPRO software.

**Figure S29.** Dose-response curves of [Au₉(TPPMS)₈]Cl₃ on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.

**Figure S30.** Dose-response curves of [Au₉(DPPBA)₈]Cl₃ on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
**Figure S31.** Dose-response curves of DPPBA on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.

**Figure S32.** Dose-response curves of TPPMS on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
CYTOTOXICITY OF AuNCs AGAINST A549 CELLS.

Figure S33. Dose-response curves of [Au₉(TPPMS)₈]Cl₃ on A549 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.

Figure S34. Dose-response curves of [Au₉(DPPBA)₈]Cl₃ on A549 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
Figure S35. Dose-response of TPPMS on A549 cells. Each data point was the average of 3 repeats. Data are insufficient to fit a sigmoidal curve.

Figure S36. Dose-response of DPPBA on A549 cells. Each data point was the average of 3 repeats. Data are insufficient to fit a sigmoidal curve.

REFERENCES