Electronic Supplementary Information

Synthesis and Solution Isomerization of Water-Soluble Au$_9$ Nanoclusters Prepared by Nuclearity Conversion of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]Cl
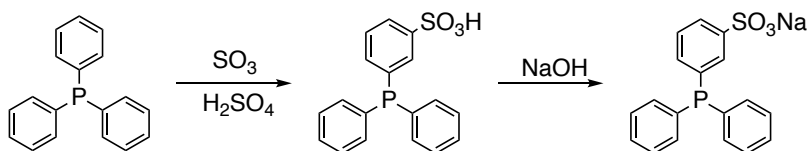
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### Contents

SYNTHESES

Synthesis of triphenylphosphine monosulfonate (TPPMS)

Scheme S1. Synthesis of triphenylphosphine monosulfonate (TPPMS).

Synthesis of TPPMS followed a reported procedure.[1] Fuming sulfuric acid (6 mL, 18-24% SO$_3$) 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 triphenylphosphine (PPh$_3$) (2.0 g, 7.6 mmol) was added rapidly. The reaction mixture was kept at 0 °C until PPh$_3$ 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 PPh$_3$. 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%).
^{1}H NMR (400 MHz, D$_2$O): δ 7.69 (d, *J* = 7.16 Hz, 1H), 7.64 (d, *J* = 7.55 Hz, 1H), 7.17 (m, 12H). ^{31}P NMR (162 MHz, D$_2$O): δ – 5.63 (s).

Synthesis of triphenylphosphine gold (I) chloride (Au(PPh$_3$)Cl)

$$HAuCl_4 \; + \; PPh_3 \; + \; H_2O \xrightarrow{\text{EtOH}} Au(PPh_3)Cl \; + \; 3\,HCl \; + \; O{=}PPh_3$$
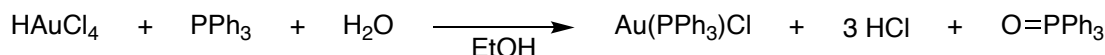
Scheme S2. Synthesis of Au(PPh$_3$)Cl.

Synthesis of Au(PPh$_3$)Cl followed a literature protocol.[2] Argon was bubbled into 95% ethanol for 15 min prior to use. Hydrogen tetrachloroaurate trihydrate (HAuCl$_4$·3H$_2$O, 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, PPh$_3$ (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

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, R_f ~ 0.5). The final product was obtained as a white solid (0.71 g, 89%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.55 (m, 15H). ^{31}P NMR (162 MHz, CDCl$_3$): δ 33.77.
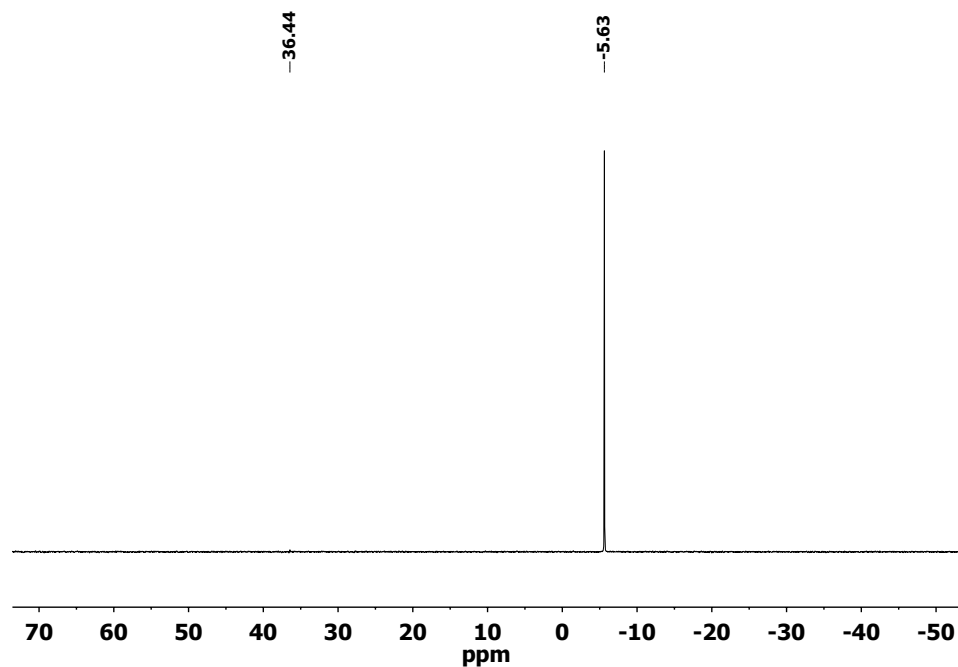
NMR SPECTRA

Figure S1. ^{31}P NMR spectrum of TPPMS in D$_2$O. A very small amount (<1%) of the oxide (36.44 ppm) is observed in the recrystallized TPPMS.
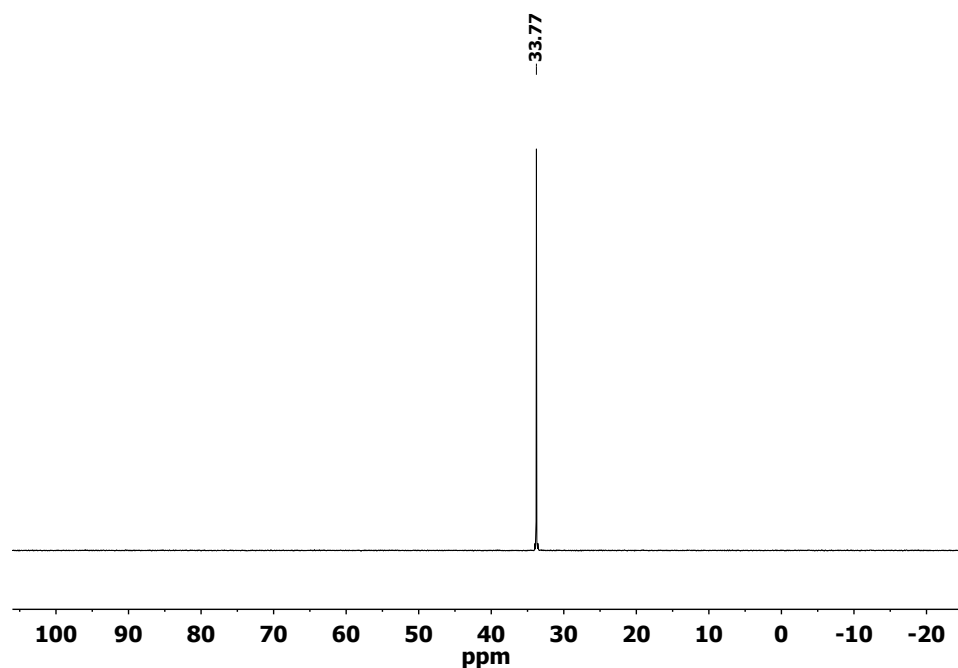
Figure S2. ^{31}P NMR spectrum of Au(PPh$_3$)Cl in CDCl$_3$.
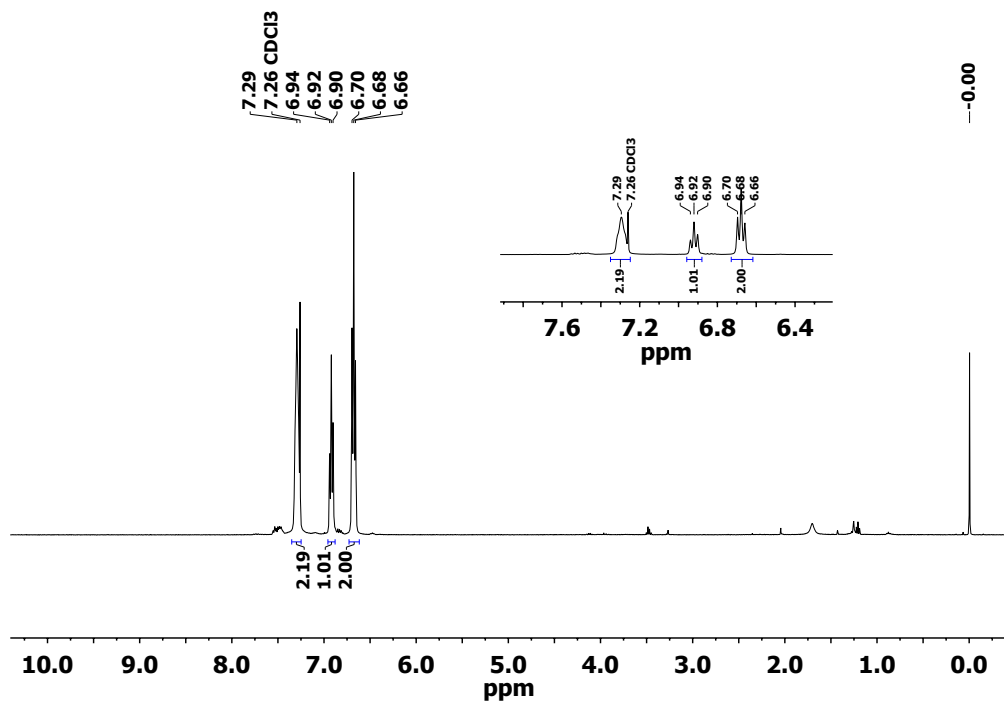
Figure S3. ^1H NMR spectrum of $[Au_{11}(PPh_3)_8Cl_2]Cl$ in $CDCl_3$.
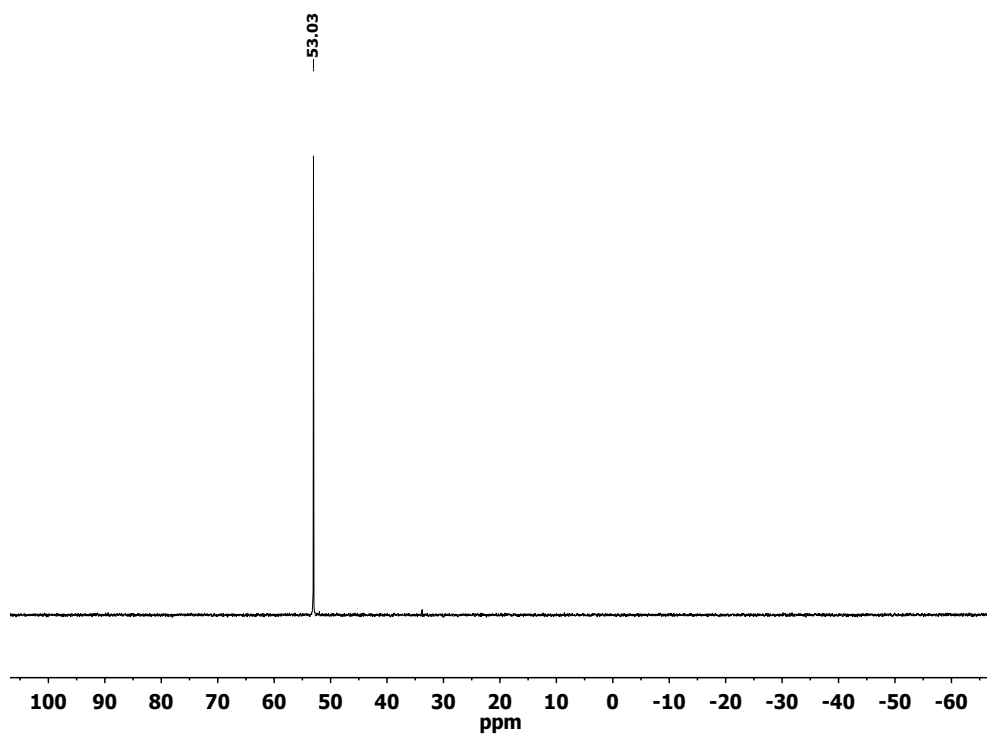
Figure S4 ^{31}P NMR spectrum of $[Au_{11}(PPh_3)_8Cl_2]Cl$ in $CDCl_3$.
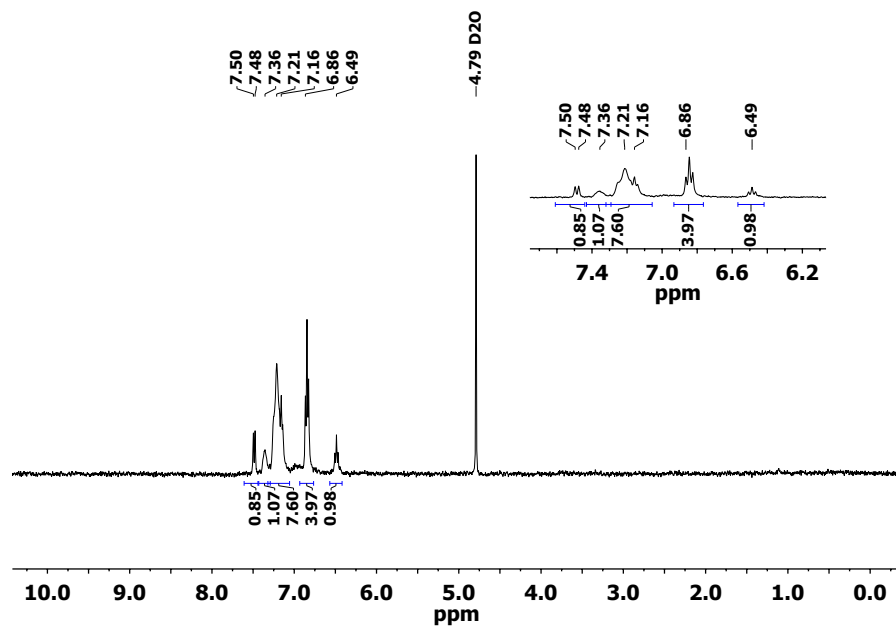
Figure S5. ^{1}H NMR spectrum of 0.6 mM of [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O.
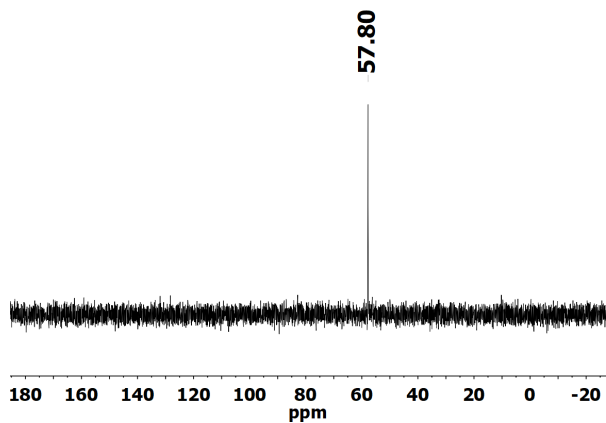
Figure S6. ^{31}P NMR spectrum of [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O.
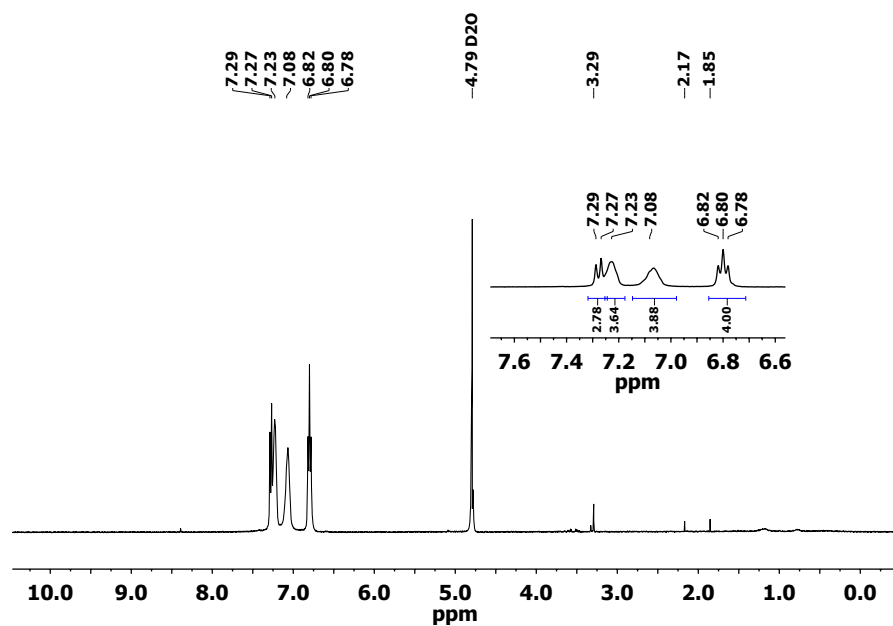
Figure S7. ^{1}H NMR spectrum of 0.6 mM of [Au$_9$(DPPBA)$_8$]Cl$_3$ in D$_2$O with 20 mM NaOH.

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57.76
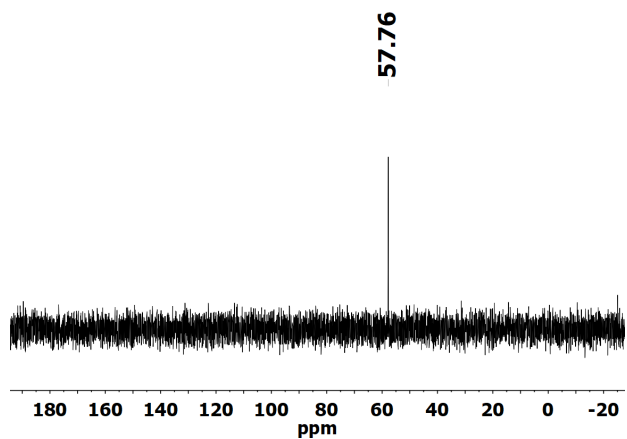
Figure S8. ^{31}P NMR spectrum of [Au$_9$(DPPBA)$_8$]Cl$_3$ in D$_2$O with 20 mM NaOH.
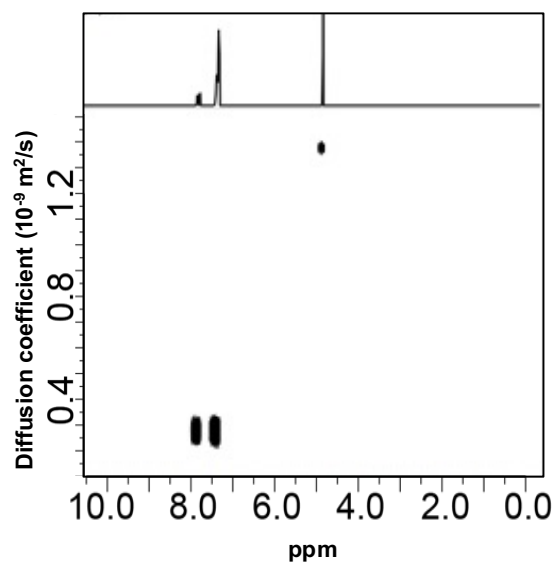
Figure S9. 2D DOSY NMR spectrum of TPPMS in D$_2$O at 289.15 K. Chemical shifts (ppm) are shown on the x-axis and the diffusion coefficients (10^{-9} m^2 s^{-1}) on the y-axis of the DOSY plot.
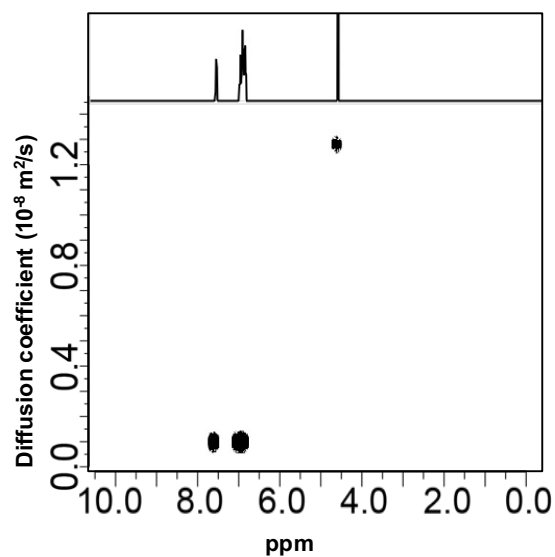
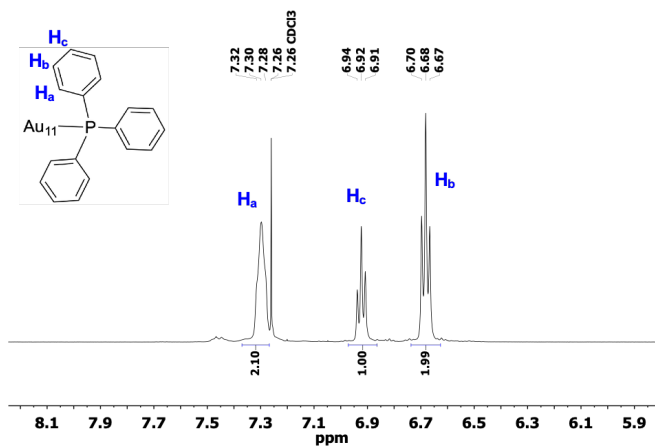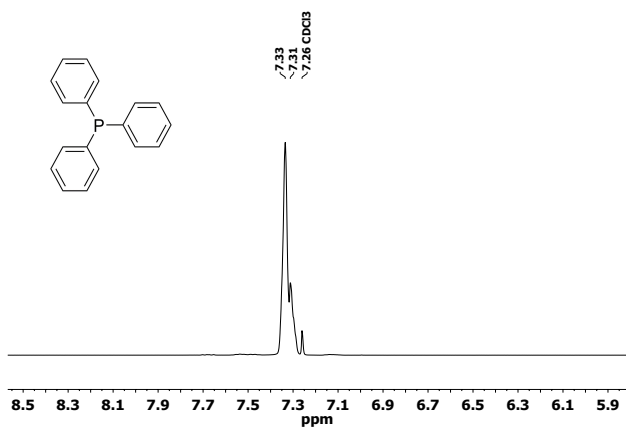**Figure S10.** 2D DOSY NMR spectrum of DPPBA in D$_2$O with 20 mM NaOH at 289.15 K. Chemical shifts (ppm) are shown on the x-axis and the diffusion coefficients (10^{-8} m^2 s^{-1}) on the y-axis of the DOSY plot.

Figure S11. ^{1}H NMR spectra of (A) PPh$_3$ and (B) [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]Cl in CDCl$_3$.

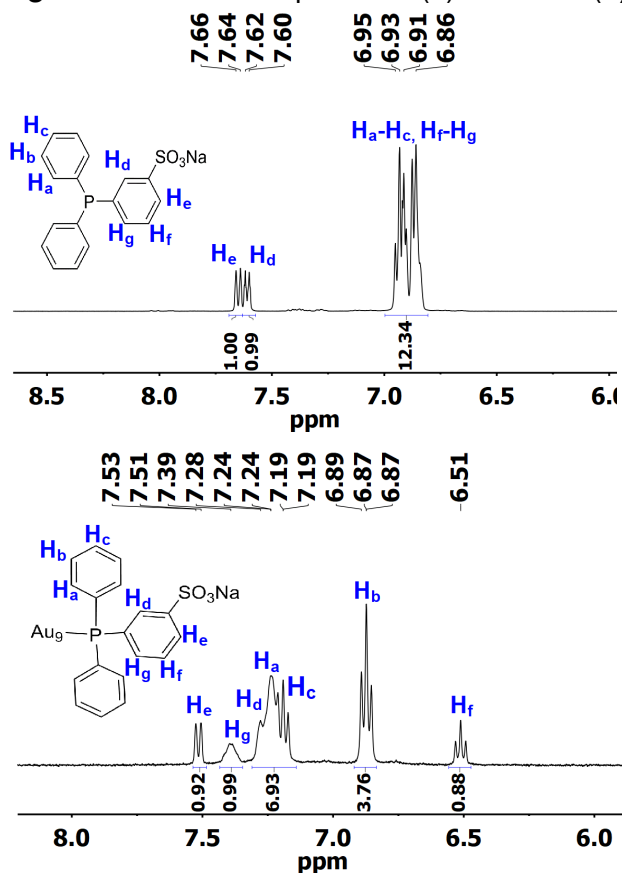**Figure S12.** ^{1}H NMR spectra of (A) TPPMS, and (B) [Au$_9$(TPPMS)$_8$]Cl$_3$ in D$_2$O. Peak assignments are aided by the 2D COSY spectrum (Fig. S14).
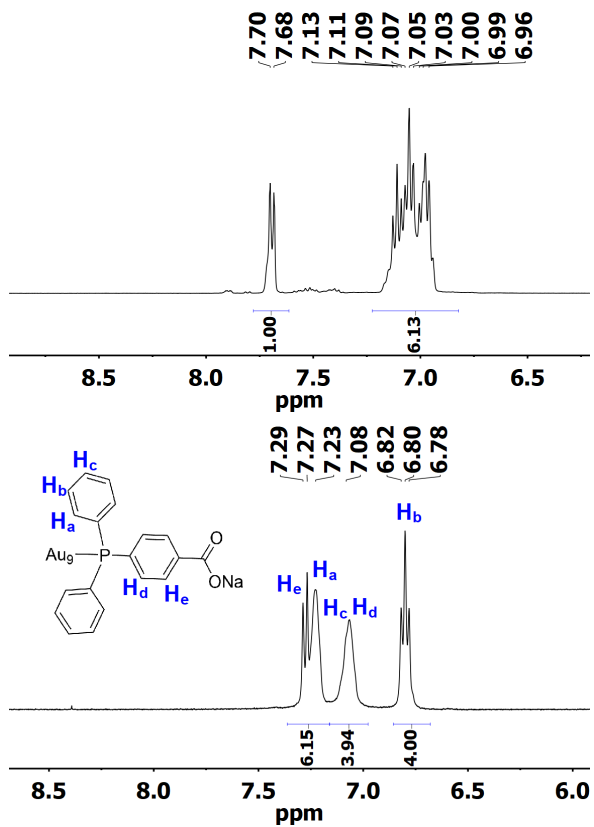
Figure S13. ^{1}H NMR spectra of (A) DPPBA and (B) [Au₉(DPPBA)₈]Cl₃ in D₂O with 20 mM NaOH. Peak assignments are aided by the 2D COSY spectrum (Fig. S15).

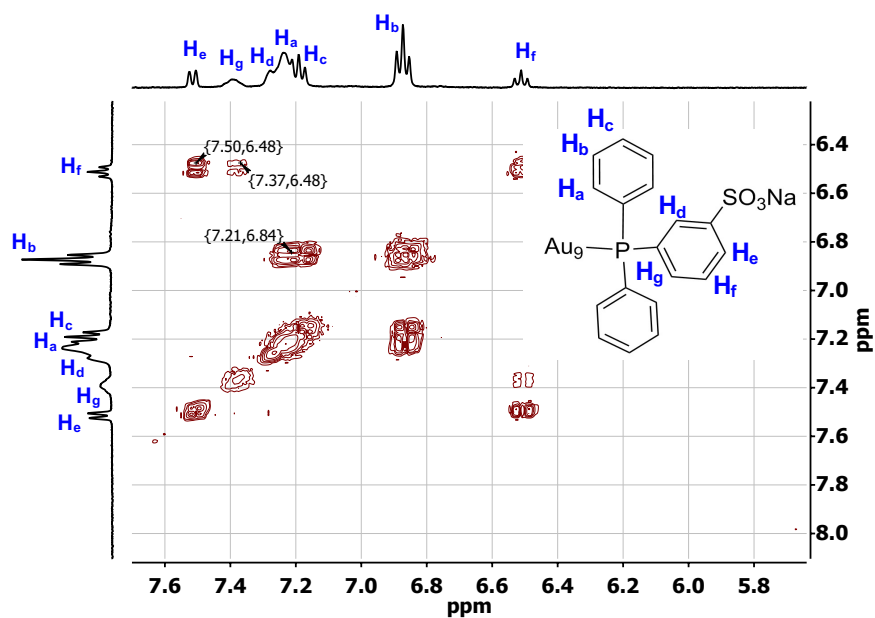**Figure S14.** [1]H-^{1}H correlation spectra (COSY) of [Au₉(TPPMS)₈]Cl₃ in D₂O.
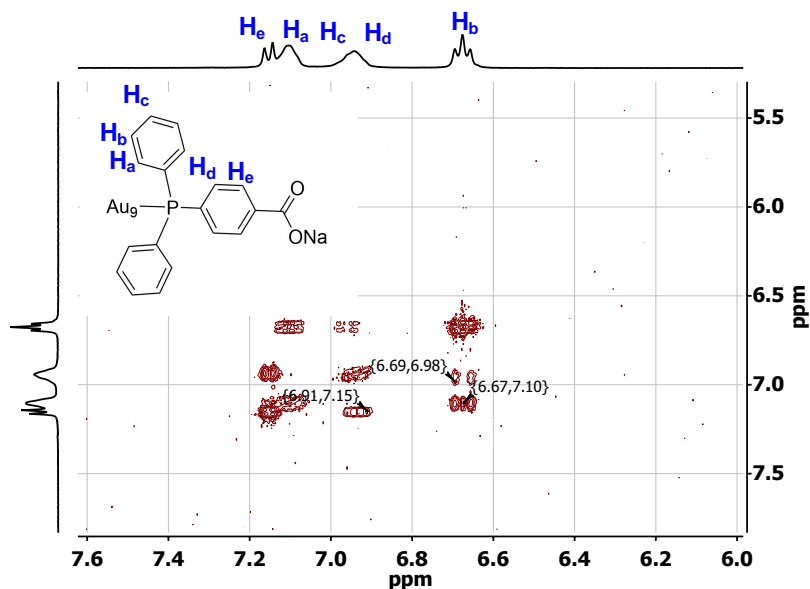
Figure S15 ^{1}H-^{1}H correlation spectra (COSY) of [Au$_9$(DPPBA)$_8$]$^{3+}$ in D$_2$O with 20 mM of NaOH.

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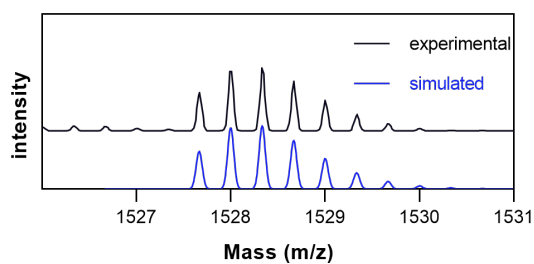
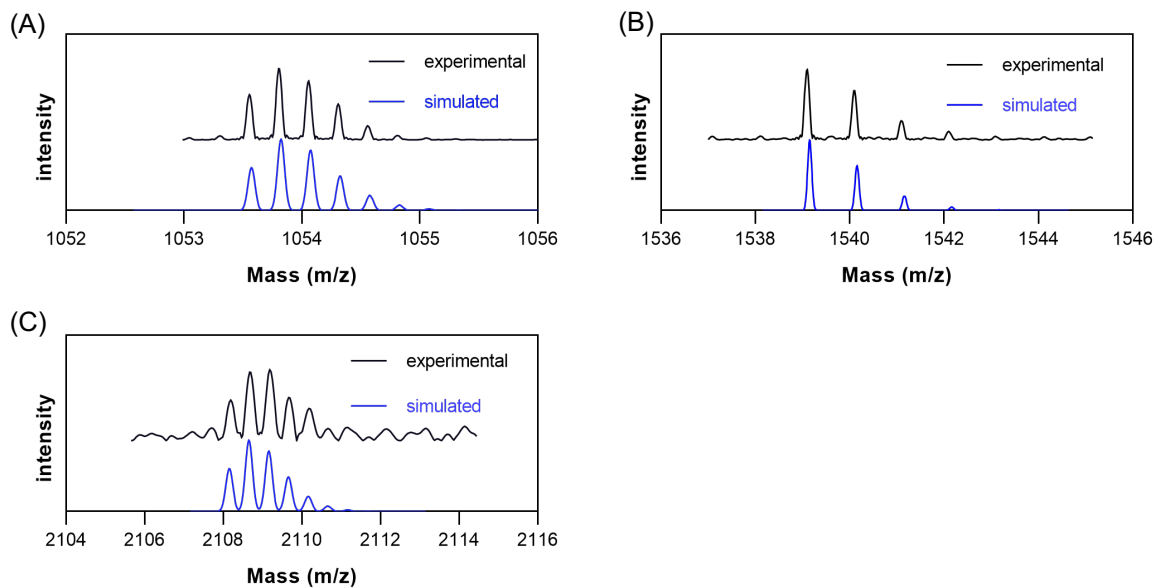**Figure S16.** Experimental and simulated isotope peak pattern overlays of for 1528.33 m/z = [Au$_9$(TPPMS)$_8$]$^{3+}$-SO$_3$Na].

Figure S17. Experimental and simulated isotope peak pattern overlays of (A) 1053.81 m/z = [Au$_9$(DPPBA)$_8$ – 7H]$^{4-}$, (B) 1539.04 m/z = [[Au$_3$(DPPBA)$_3$]$^{2-}$ + 2H + CH$_3$O$^-$]$^-$ and (C) 2108.70 m/z = [Au$_9$(DPPBA)$_8$ – 5H]$^{2-}$.

UV-VIS SPECTRA
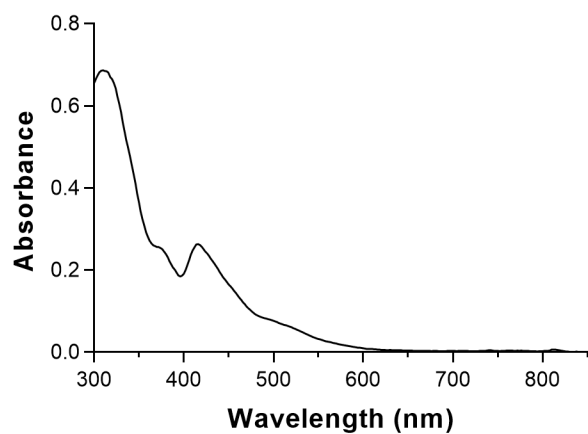
Figure S18. UV-Vis spectrum of $[Au_{11}(PPh_3)_8Cl_2]Cl$ in DCM.
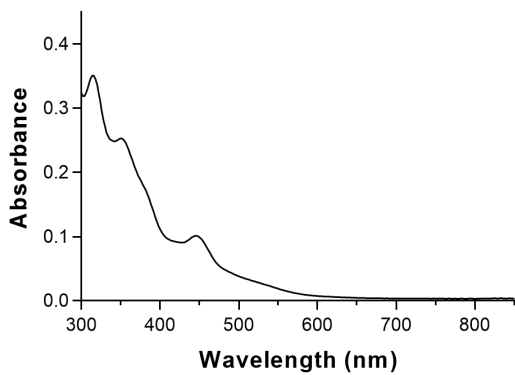

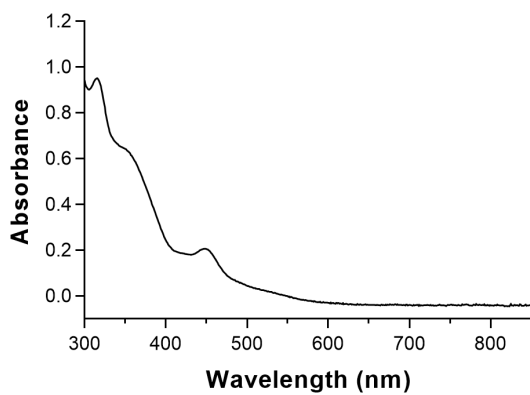**Figure S19.** UV-Vis spectrum of $[Au_9(TPPMS)_8]Cl_3$ in water (0.125 mg/mL).

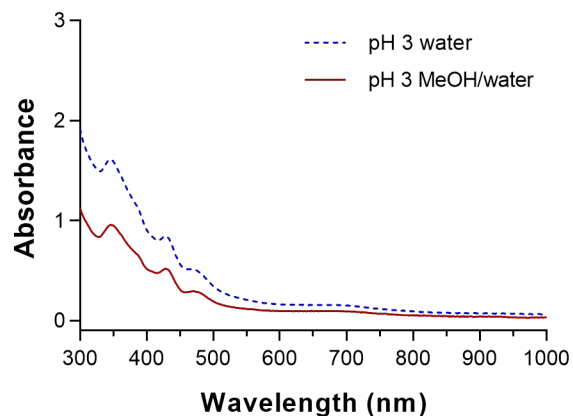**Figure S20.** UV-Vis spectrum of $[Au_9(DPPBA)_8]Cl_3$ in 20 mM NaOH (0.5 mg/mL).

Figure S21. UV-Vis spectra of [Au$_9$(DPPBA)$_8$]Cl$_3$ (0.25 mg/mL) in pH 3 water (dashed line), and in pH 3 MeOH/water (1:1) (solid line).
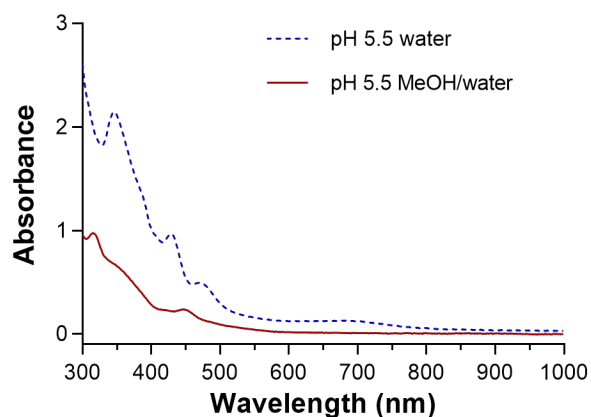

Figure S22. UV-Vis spectra of [Au$_9$(DPPBA)$_8$]Cl$_3$ (0.25 mg/mL) in pH 5.5 water (dashed line) and in pH 5.5 MeOH/water (1:1) (solid line).
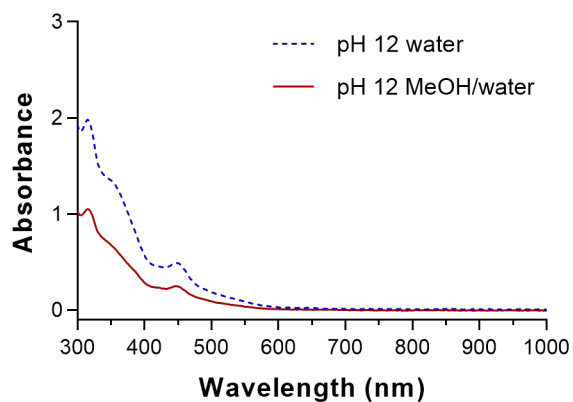

Figure S23. UV-Vis spectra of [Au$_9$(DPPBA)$_8$]Cl$_3$ (0.25 mg/mL) in pH 12 water (dashed line) and in pH 12 MeOH/water (1:1) (solid line).
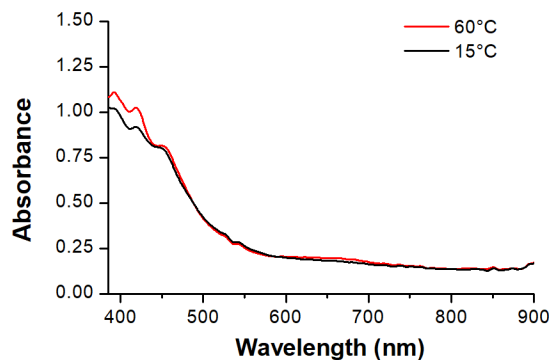
Figure S24. Absorption spectra of [Au$_9$(DPPBA)$_8$]Cl$_3$ in EtOH (20 mM NaOH), immediately after heating to 60 °C (red line) and after cooling to 15 °C (black line). The spectra were smoothed using an FFT filter function in OriginPRO to reduce noise.
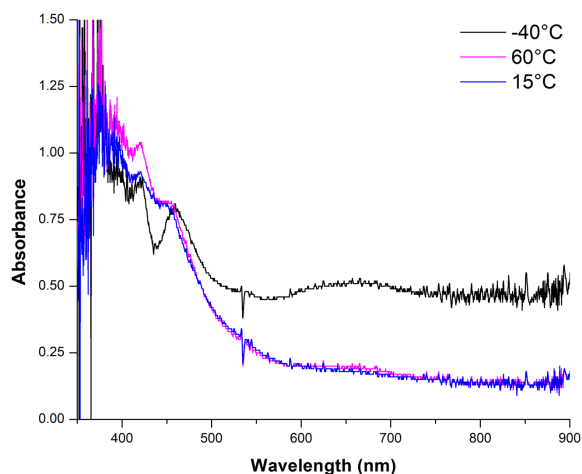

Figure S25. Raw Vis-NIR absorption spectra of Au$_9$(DPPBA)$_8$Cl$_3$ in ethanol. An artifact present at 535 nm arises from the light source.

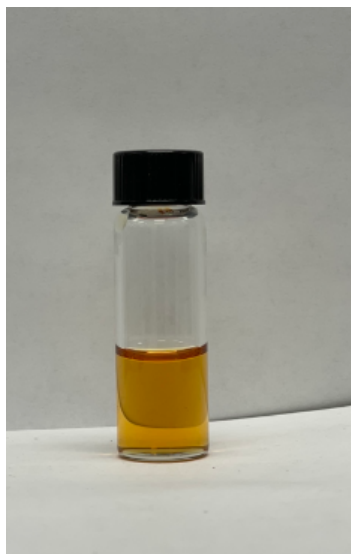**Figure S26.** Au$_9$(TPPMS)$_8$Cl$_3$ in conc. HCl (86%, 9 M). No color change was detected. The suspension turned into a completely clear solution after 2 days.

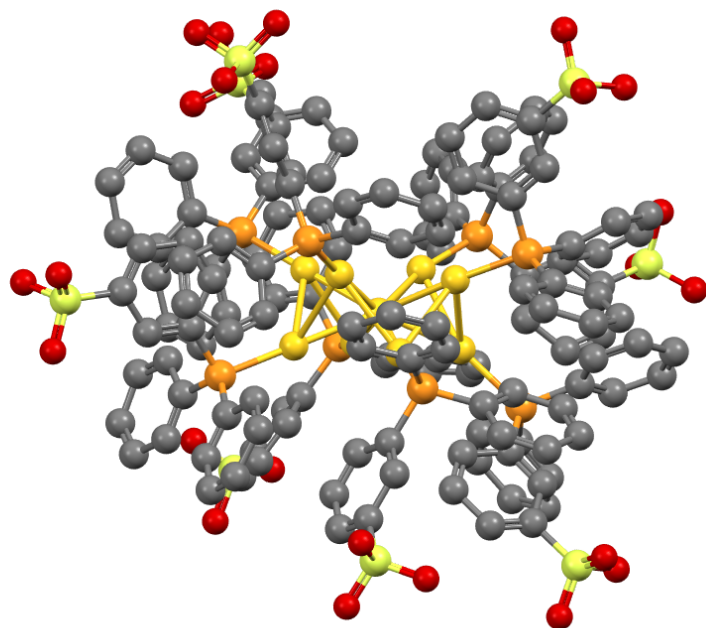**PROPOSED STRUCTURES OF WATER-SOLUBLE [AU$_9$(L)$_8$]$^{3+}$**

Figure S27. Proposed C_4 'crown' isomer structure of Au$_9$(TPPMS)$_8$Cl$_3$. 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(C$_6$H$_4$OMe-p)$_3$ ligands in the C_4 isomer in Ref. 3 (*cf* **Fig. 1A**) with TPPMS and minimizing the energy using the Universal force field algorithm (UFF) in Avogadro software.
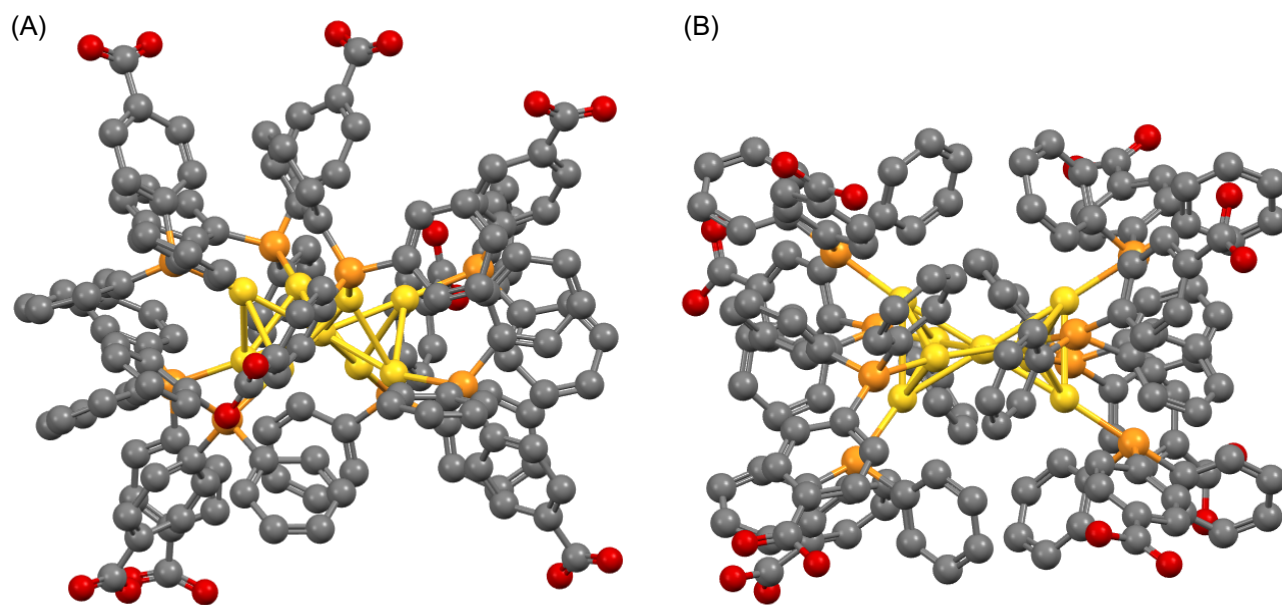
(A)   (B)

Figure S28. Proposed structure of Au$_9$(DPPBA)$_8$Cl$_3$ as (A) the C_4 (crown) isomer and (B) the D_{2h} (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(C$_6$H$_4$OMe-p)$_3$ ligands with DPPBA in the C_4 and D_{2h} 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.

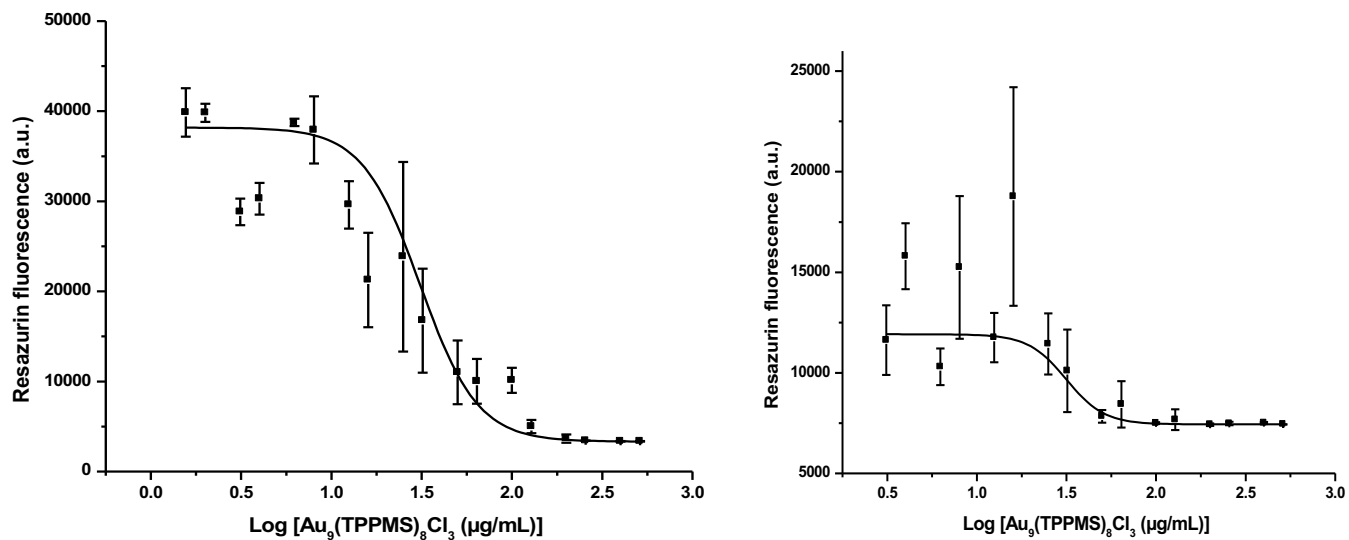Dose response curves were fitted using OriginPRO software.

Figure S29. Dose-response curves of $[Au_9(TPPMS)_8]Cl_3$ on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
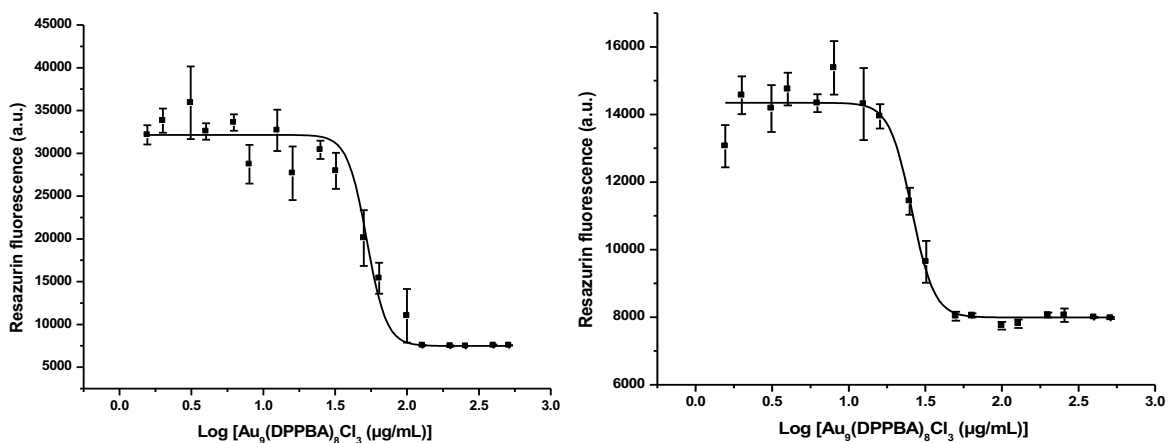

Figure S30. Dose-response curves of $[Au_9(DPPBA)_8]Cl_3$ on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
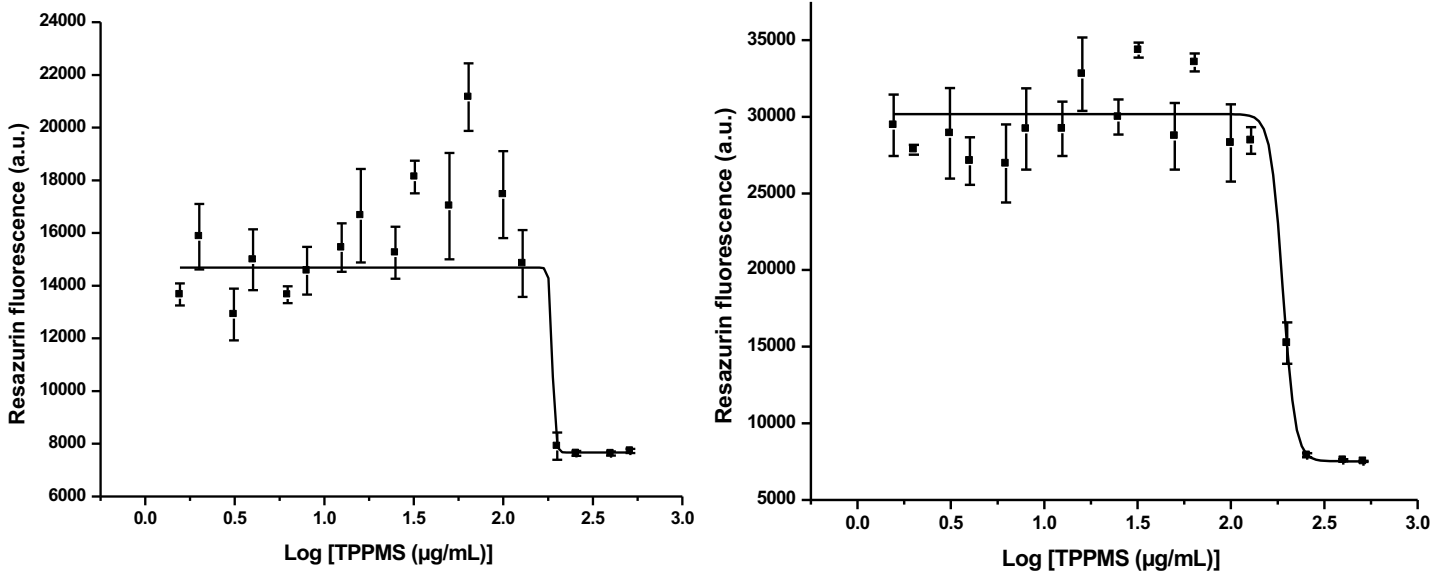
Figure S31. Dose-response curves of DPPBA on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
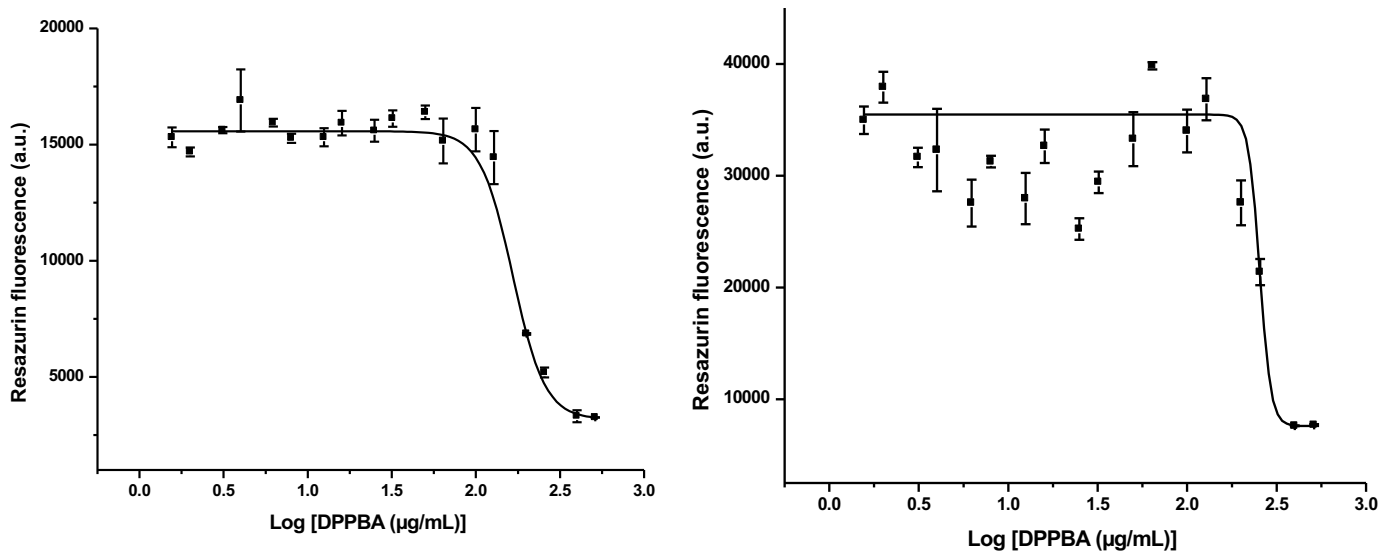

Figure S32. Dose-response curves of TPPMS on 3T3 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
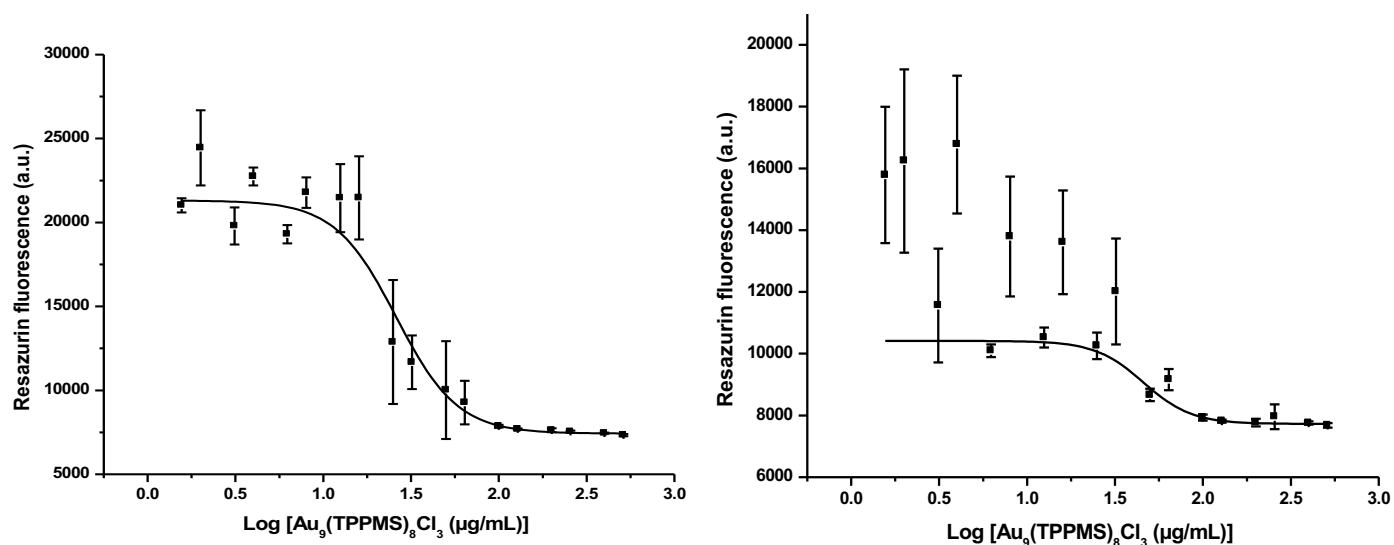
CYTOTOXICITY OF AuNCs AGAINST A549 CELLS.

Figure S33. Dose-response curves of $[Au_9(TPPMS)_8]Cl_3$ on A549 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
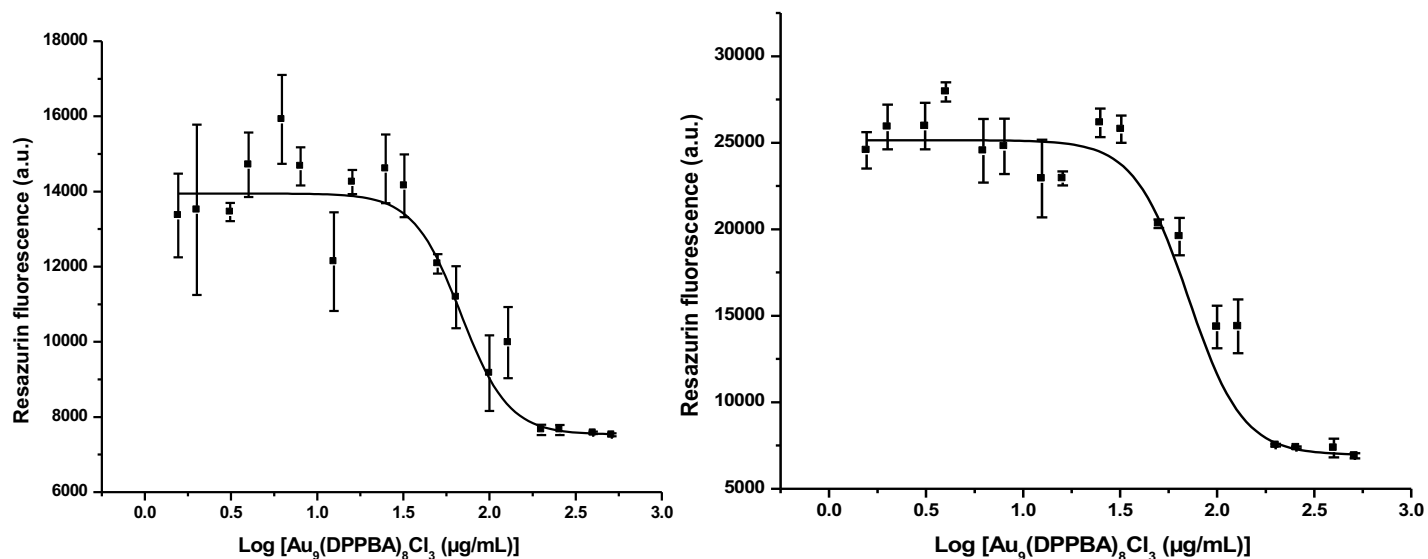

Figure S34. Dose-response curves of $[Au_9(DPPBA)_8]Cl_3$ on A549 cells: experimental data (solid squares) and the fits (lines). Each data point was the average of 3 repeats.
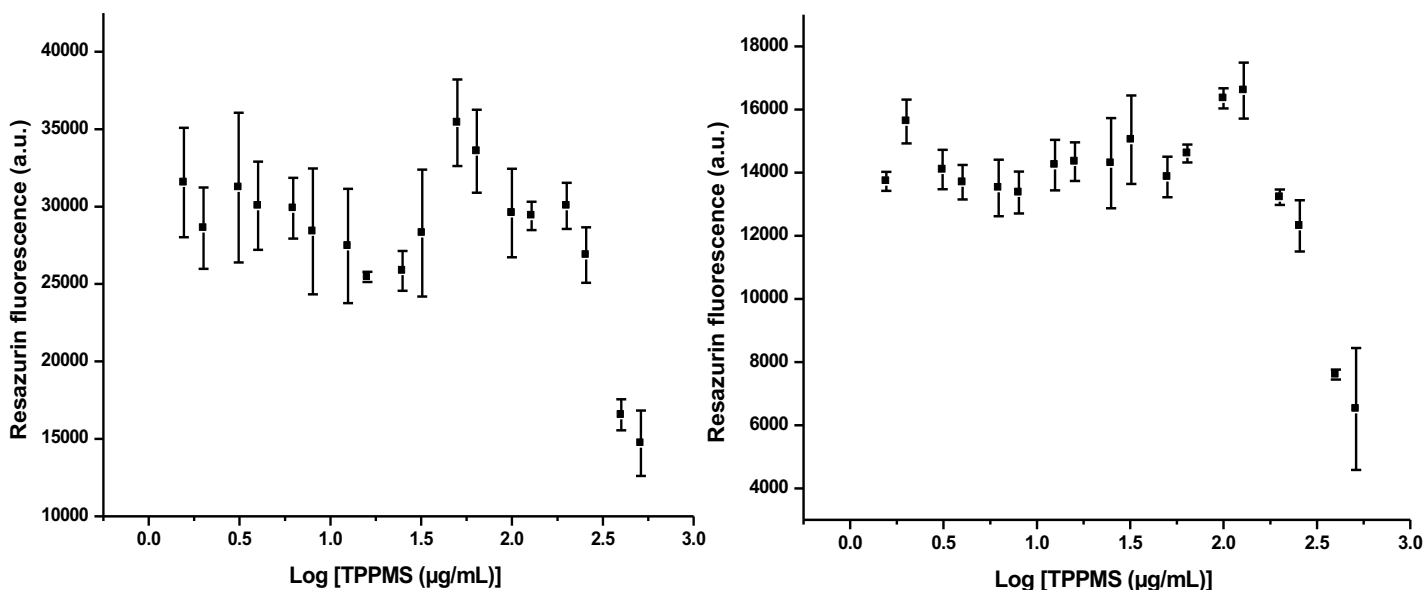
Figure S35. Dose-response of TPPMS on A549 cells. Each data point was the average of 3 repeats. Data are insufficient to fit a sigmoidal curve.
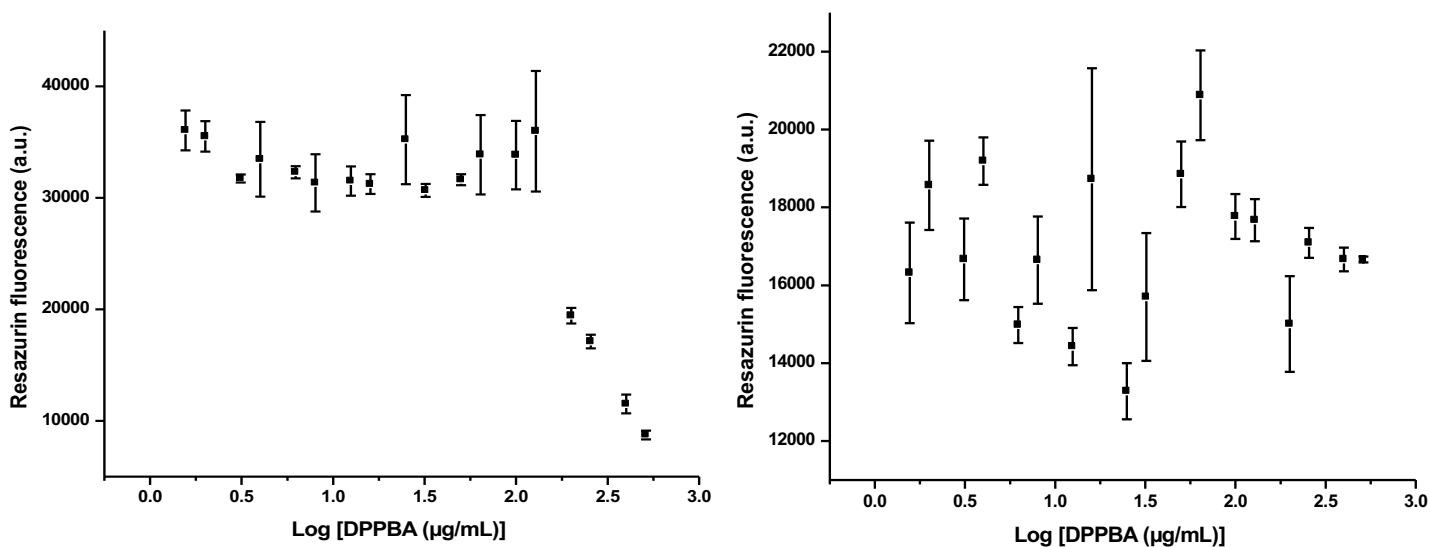

Figure S36. Dose-response of DPPBA on A549 cells. Each data point was the average of 3 repeats. Data are insufficient to fit a sigmoidal curve.

REFERENCES

1.   Karschin, A.; Kläui, W.; Peters, W.; Spingler, B., *Eur. J. Inorg. Chem.* **2010,** *2010* (6), 942-946.
2.   Braunstein, P.; Lehner, H.; Matt, D.; Burgess, K.; Ohlmeyer, M. J., *Inorg. Synth.* **1990,** *10*, 218-221.
3.   Briant, C. E.; Hall, K. P.; Mingos, D. M. P., *J. Chem. Soc., Chem. Commun.* **1984,** (5), 290-291.