

**Supporting Information:**

**Hydride, Chloride, and Bromide Show Similar**

**Electronic Effects in the  $\text{Au}_9(\text{PPh}_3)_8^{3+}$**

**Nanocluster**

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# Materials and methods

## *Materials*

Chemicals were used as received without further purification, and all reactions were conducted under ambient conditions. Precursor complex and cluster syntheses were performed using 98% sodium borohydride, 99% triphenylphosphine, and 99% AgNO<sub>3</sub> purchased from Oakwood Chemical. Gold precursor complexes and nanoclusters were prepared from 99.995% chloroauric acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) purchased from Alfa Aesar. Reactions were carried out in ACS grade reagent alcohol, acetone, dichloromethane, diethyl ether, or methanol purchased from VWR. ESI-MS was performed using UHPLC grade methanol purchased from Fisher Chemical. CDCl<sub>3</sub> was purchased from Cambridge Isotope Laboratories.

## *Synthesis of chloro(triphenylphosphine)gold(I)*

HAuCl<sub>4</sub>·3H<sub>2</sub>O (200 mg, 0.508 mmol) was dissolved in 5 mL of reagent alcohol under vigorous stirring to form a yellow solution. Triphenylphosphine (360 mg, 1.37 mmol) was ground into a fine powder, dissolved in 10 mL of reagent alcohol by sonication, and dispensed quickly into the HAuCl<sub>4</sub>·3H<sub>2</sub>O solution. A white powder immediately precipitated from the reaction mixture, which continued to stir for 15 minutes. The crude solid was collected by vacuum filtration and dried, giving an 80% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K)  $\delta$ /ppm: 7.52 (15H, m).

## *Synthesis of (triphenylphosphine)gold(I) nitrate*

Chloro(triphenylphosphine)gold(I) (30.0 mg, 0.061 mmol) was added to 15 mL of dichloromethane and stirred. Separately, AgNO<sub>3</sub> (10.4 mg, 0.061 mmol) was suspended in 5 mL of methanol and brought to a boil to solubilize the silver salt. The hot AgNO<sub>3</sub> solution was then added dropwise to the gold-containing mixture at room temperature. During the addition, a white precipitate slowly forms. After 30 minutes, the mixture was vacuum filtered and the supernatant rotovaped to dryness to give the final product with a 79% yield. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, 400 MHz, 298 K)  $\delta$ /ppm: 7.66 (15H, m)

## *Synthesis of triphenylphosphine-protected gold nanoclusters*

(Triphenylphosphine)gold(I) nitrate (25 mg, 0.048 mmol) was dissolved in 10 mL of methanol and stirred. Sodium borohydride (4.0 mg, 0.105 mmol) was then added as a solid and the reaction mixture immediately changed from clear to dark orange. The reaction was stirred for one hour, rotovaped to dryness, and used without further purification. Nominally, the predominant species synthesized is  $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$ .

### ***Addition of hydride, chloride, or bromide to $\text{Au}_9(\text{PPh}_3)_8^{3+}$***

The clusters  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$ ,  $\text{Au}_9(\text{PPh}_3)_8\text{Cl}^{2+}$ , and  $\text{Au}_9(\text{PPh}_3)_8\text{Br}^{2+}$  were each prepared by electrospray and only isolated in gas phase. All three clusters were prepared by co-spraying the appropriate precursor (vide infra) with 20  $\mu\text{L}$  of 1 mg/mL unpurified gold nanocluster solution (prepared in UHPLC grade methanol) and diluting to 250  $\mu\text{L}$  with UHPLC-grade methanol.  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$ ,  $\text{Au}_9(\text{PPh}_3)_8\text{Cl}^{2+}$ , and  $\text{Au}_9(\text{PPh}_3)_8\text{Br}^{2+}$  were obtained by co-spraying with 20  $\mu\text{L}$  of 1 mM borane tert-butylamine, 25  $\mu\text{L}$  of 1 mM tetraphenylphosphonium chloride, and 10  $\mu\text{L}$  of 1 mM tetrabutylammonium bromide, respectively.

## **Characterization**

### ***Electrospray Ionization Mass Spectrometry***

Characterization of the product distributions were performed using an Agilent 6224 electrospray ionization/time-of-flight mass spectrometer. The heater on the source inlet was maintained at 150°C, ions were sprayed at 2.5 kV using  $\text{N}_2$  carrier gas. Solutions of the raw synthetic mixture of gold nanoclusters were prepared using UHPLC grade methanol and analyzed at a concentration of 100  $\mu\text{g}/\text{mL}$ .

Table S1: Mass spectral characterization of  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$ ,  $\text{Au}_9(\text{PPh}_3)_8\text{Cl}^{2+}$ , and  $\text{Au}_9(\text{PPh}_3)_8\text{Br}^{2+}$ .

	Measured m/z	Calculated m/z	Normalized Abundance	Calculated Abundance
$\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$	1935.21	1935.22	0.57	0.64
	1935.71	1935.72	1.00	1.00
	1936.21	1936.22	0.78	0.79
	1936.72	1936.72	0.40	0.41
	1937.22	1937.22	0.18	0.16
	1937.71	1937.73	0.08	0.05
	1938.22	1938.23	0.04	0.01
$\text{Au}_9(\text{PPh}_3)_8\text{Cl}^{2+}$	1952.26	1952.20	0.56	0.64
	1952.76	1952.70	1.00	1.00
	1953.26	1953.20	0.94	0.98
	1953.76	1953.70	0.72	0.72
	1954.26	1954.20	0.40	0.40
	1954.75	1954.70	0.15	0.18
	1955.28	1955.20	0.02	0.06
$\text{Au}_9(\text{PPh}_3)_8\text{Br}^{2+}$	1974.22	1974.17	0.45	0.46
	1974.73	1974.67	0.73	0.72
	1975.23	1975.17	0.94	1.00
	1975.73	1975.67	1.00	0.98
	1976.23	1976.18	0.69	0.65
	1976.73	1976.68	0.38	0.32
	1977.22	1977.18	0.11	0.12

***Mass-selective photofragmentation UV/Vis spectroscopy***

Our experiment has been described in detail in a previous publication, but a brief description will be given here.<sup>S1</sup> Mass-selective photofragmentation UV/Vis spectra were acquired using a home-built electrospray ionization/time-of-flight mass spectrometer equipped with a cryogenically-cooled octopole ion trap. Wet-chemically synthesized gold nanoclusters are introduced into the instrument by electrospray ionization and directed to the cryogenic ion trap containing He buffer gas and maintained at 3.8 K. The gold cluster are sympathetically cooled by the buffer gas upon which we observe condensation of  $\approx 20$  He atoms onto the clusters. Ions are stored and cooled for 45 ms, after which a single pulse of light from a tunable optical parametric oscillator (GWU versaScan/uvScan, 258 – 2600 nm range) pumped by the third harmonic of an Nd:YAG laser (Spectra-Physics Quanta-Ray Lab 150-30H; 20 Hz, 2.5 W) is directed into the ion trap. Loss of all bound He occurs if the laser wavelength is on resonance with an electronic transition, whereas no change in the tagging distribution is

measured off resonance. All ions are then extracted out of the trap, orthogonally accelerated, and separated by mass-to-charge using time-of-flight. The laser-power corrected fraction of He-free ions is determined as a function of wavelength to construct an absorption spectrum. Critically, only a single photon is required for this process, yielding spectra that are linearly and thus directly comparable to standard solution-phase UV/vis spectra. The output power of the OPO is controlled (10 – 100  $\mu\text{J}/\text{pulse}$ ) such that no more than 10% tag-loss is measured in order to avoid spectral saturation and multiphoton effects. Figure S1 shows sample mass spectra of for He-tagged  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  before and after illumination with 600 nm.

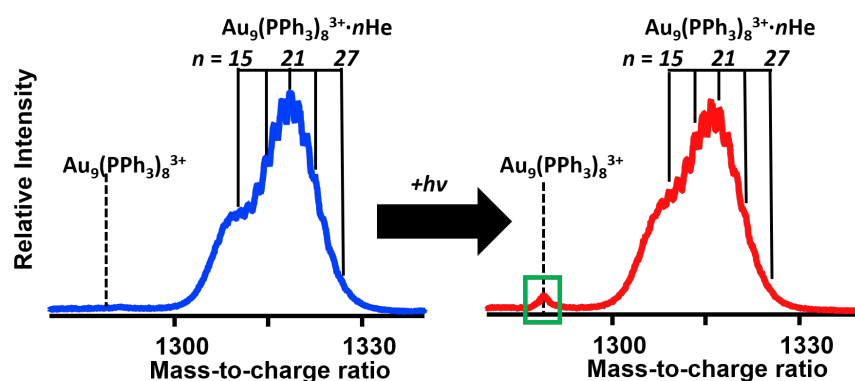


Figure S1: He-tagged  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  before (left) and after (right) irradiation with 600 nm light ( $E_{\text{pulse}} = 100 \mu\text{J}$ ). The ratio of the small untagged signal, highlighted in green, to the large tagged signal, after laser power normalization, yields the spectra reported here.

## Comparison with $\text{Au}_9(\text{P}(\text{p-OCH}_3\text{-Ph})_3)_8^{3+}$

Crystallographic analysis reveals that the  $\text{Au}_9(\text{P}(\text{p-OCH}_3\text{-Ph})_3)_8^{3+}$  cluster adopts a  $D_{4d}$  core symmetry, a geometry closely related to the  $C_{4v}$  core structure predicted by density functional theory for  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$ .<sup>S2,S3</sup> Figure S2 presents the UV/Vis spectra for these two clusters along with  $\text{Au}_9(\text{PPh}_3)_8^{3+}$ . Our measurements show that the  $\text{Au}_9(\text{P}(\text{p-OCH}_3\text{-Ph})_3)_8^{3+}$  and  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$  clusters exhibit unique electronic absorption spectra with no obvious shared pattern, indicating that geometry alone does not account for the remarkable evolution in electronic structure upon hydride ligation.

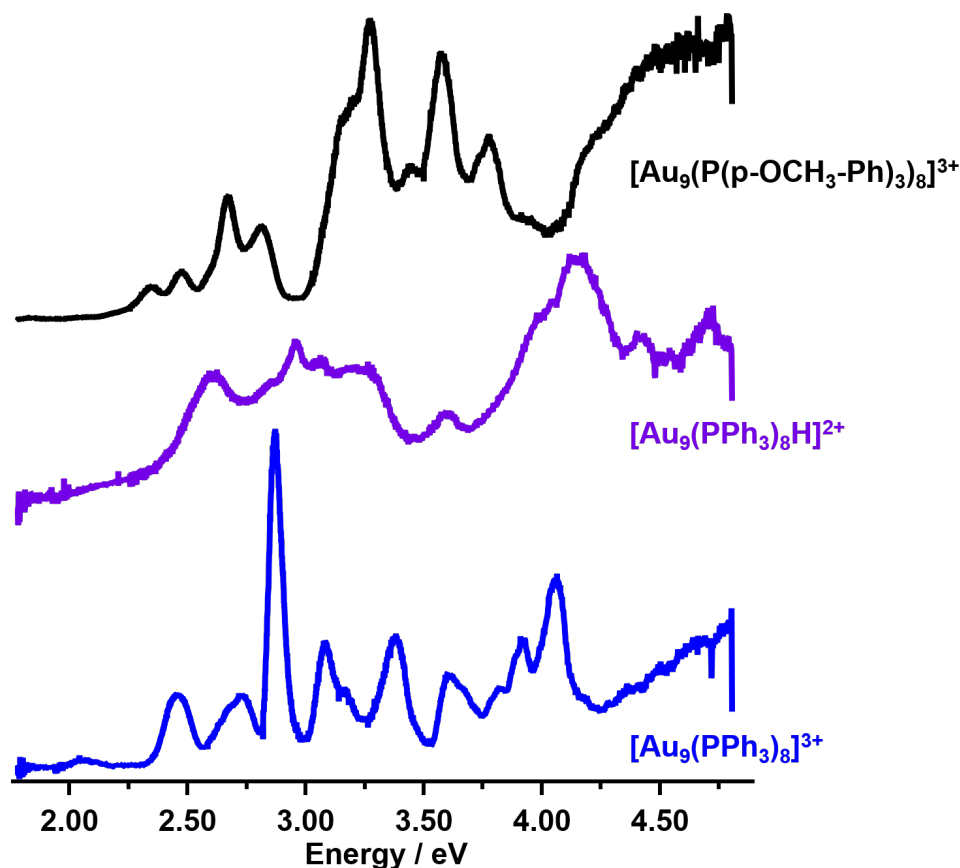


Figure S2: Comparison of the  $\text{Au}_9(\text{P}(\text{p-OCH}_3\text{-Ph})_3)_8^{3+}$  (black),  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$  (violet), and  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  (blue) UV/Vis spectra.

## Comparison between gas- and solution-phase $\text{Au}_9(\text{PPh}_3)_8^{3+}$ and $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$

The solution-phase spectra for  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$  (blue) and  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  (red) are presented in Figure S3. Work by Tsukuda and co-workers suggest that upon introduction of hydride to  $\text{Au}_9(\text{PPh}_3)_8^{3+}$ , the ion binds covalently to the core. Surprisingly, a close correspondence of the clusters in the two phases is observed which suggests that the hydride binds covalently in the gas phase. Furthermore, given the spectral similarity between the chloride- and bromide-substituted  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  clusters to the hydride, our data is consistent with covalent attachment of the halides.

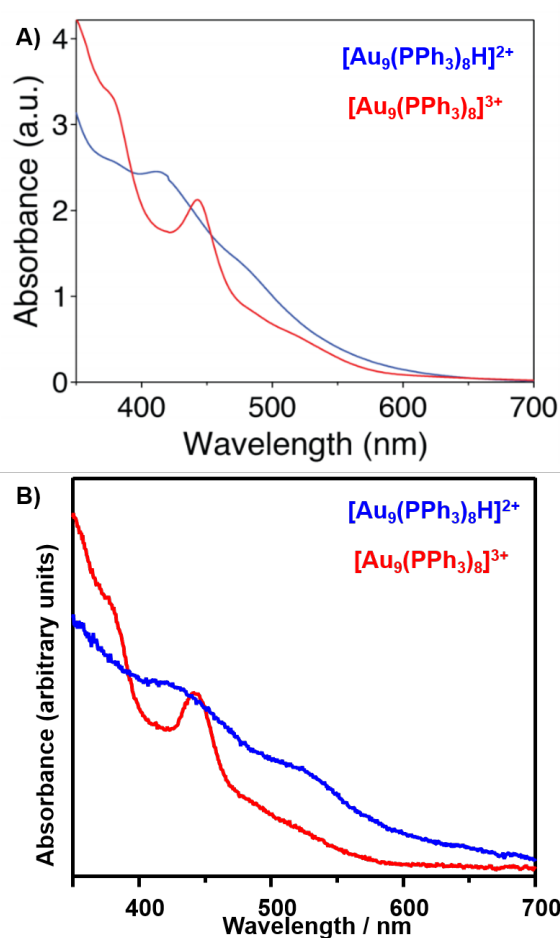


Figure S3: Comparison of the  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$  (blue) and  $\text{Au}_9(\text{PPh}_3)_8^{3+}$  (red) UV/Vis spectra in units of wavelength. Panel A) shows the spectra acquired by Tsukuda and co-workers and B) are the solution-phase spectra of clusters prepared in our lab. A 1  $\mu\text{M}$  solution of  $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$  in methanol was mixed with 1 mg of  $\text{NaBH}_4$  to produce  $\text{Au}_9(\text{PPh}_3)_8\text{H}^{2+}$ . Fig. S3A was adapted with permission from Reference S3. Copyright 2018 American Chemical Society.

## References

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