

## Supporting Information For

### Electronic Transitions in Highly Symmetric Au<sub>130</sub> Nanoclusters by Spectroelectrochemistry and Ultrafast Spectroscopy

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**Table-S1.** Potential and peak spacing of the main QDL features of the Au<sub>130</sub> cluster.

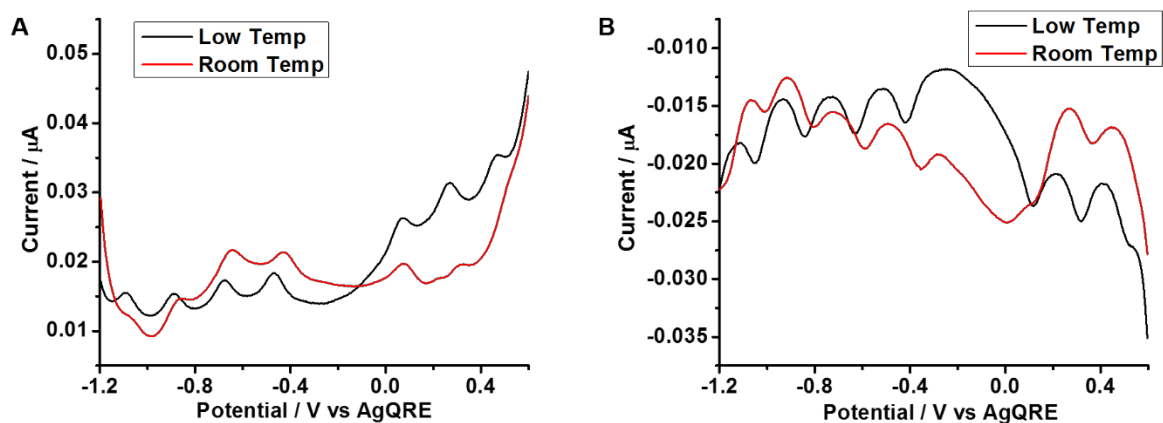
<b>Oxidation (V)</b>	-1.32	-1.15	-0.97	-0.74	-0.51		-0.01	0.21	0.42	0.6	0.79	0.96
<b>Peak Spacing</b>		0.17	0.18	0.23	0.23			0.22	0.21	0.18	0.19	0.17
<b>Reduction (V)</b>	-1.33	-1.15	-0.97	-0.73	-0.51		-0.01	0.22	0.43	0.62	0.78	0.96
<b>Peak Spacing</b>		0.18	0.18	0.24	0.22			0.23	0.21	0.19	0.16	0.18

The peak spacing values are calculated by subtracting the neighboring (Right-Left) values in the row above. Highlighted peaks represent the 0.5 V band gap discussed in the main text. The open circuit potential (OCP) during the time of these measurements was 0.0 V.

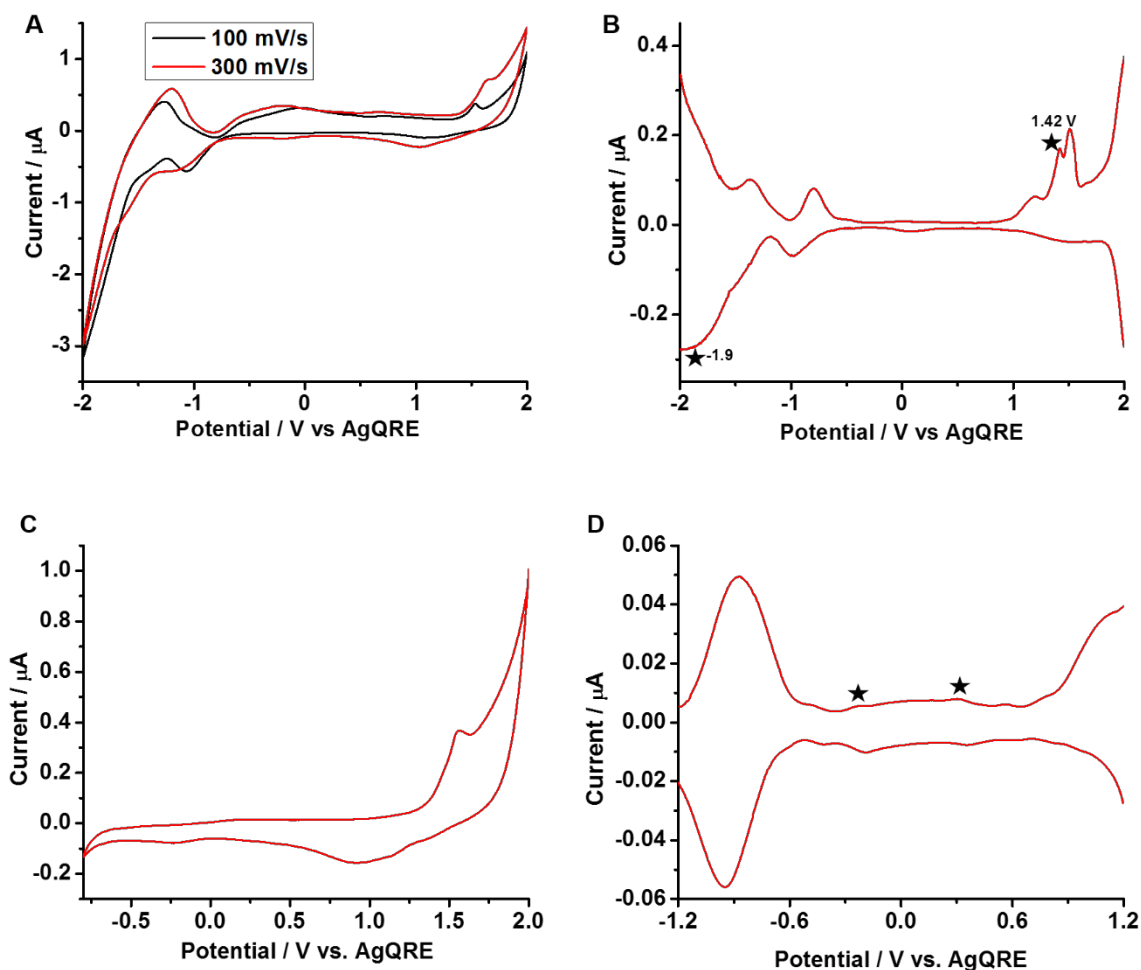
**Table-S2. Calculations of the Observed Transitions in the Differential Spectrum in CH<sub>2</sub>Cl<sub>2</sub>**

Differential Spectrum			Electrochemistry			Expected Changes by Ox/Red (Inc. +; Dec. -)
(nm)	(eV)	Changes in $\Delta$ Abs.	Low E (LE, V)	High E (HE, V)	Transition (LE - HE)	
<b>371</b>	<b>3.34</b>	Oxidation (-) Reduction (+)				SS
371	3.34		1.46	-1.90	3.36	Ox (-); Red (+)
<b>490</b>	<b>2.58</b>					SS
490	2.58		0.29	-2.29	2.58	Ox (-); Red (+)
		Isosbestic Point	2.22	-0.21	2.43	Red (-)
530	2.34		0.08	-2.29	2.37	Ox (-); Red (+)
			2.22	0.00	2.22	0
560	2.21		0.29	-1.90	2.19	0
580	2.14	Oxidation (+) Reduction (-)	2.22	0.08	2.14	Ox (+); Red (-)
<b>602</b>	<b>2.06</b>					SS
580	2.14		2.22	0.08	2.14	Ox (+); Red (-)
625	1.98		0.08	-1.90	1.98	Ox (-); Red (+)
644	1.93		2.22	0.29	1.93	Ox (+)
<b>700</b>	<b>1.75</b>					SS
>700	<1.75		1.46	-0.21	1.67	Red (-)
885	1.40		1.46	0.08	1.38	Ox (+); Red (-)
755	1.64	Red (+)	-0.21	-1.90	1.69	Red (+)

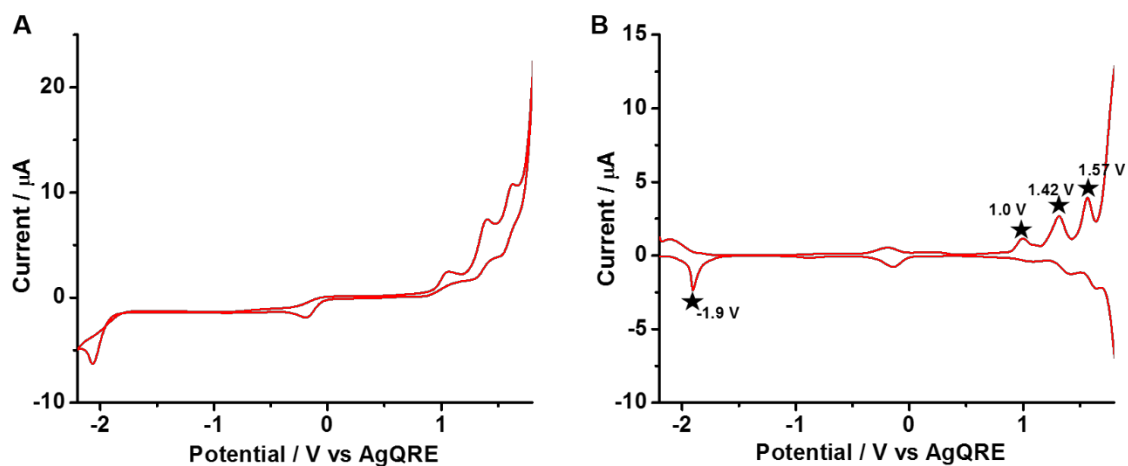
**Note:** The wavelength numbers were read from Figure 3. The OCP of the Au NCs used in the measurements was 0.18 V. Bolded blue boxes represent the four steady state features in the UV-Vis spectrum. Calculations directly below each of these areas represent transitions that either directly affect the steady state transition or are located between that steady state and the next. Some transitions (shaded in pink) are shown twice in the table (the second is shown in italics). This is due to those transitions having possible effects on more than one steady state/region in the differential spectrum. The green shaded boxes represent the isosbestic point which splits the differential spectrum into two distinct regions of overall behavior (either overall decreasing or overall increasing with oxidation/reduction).



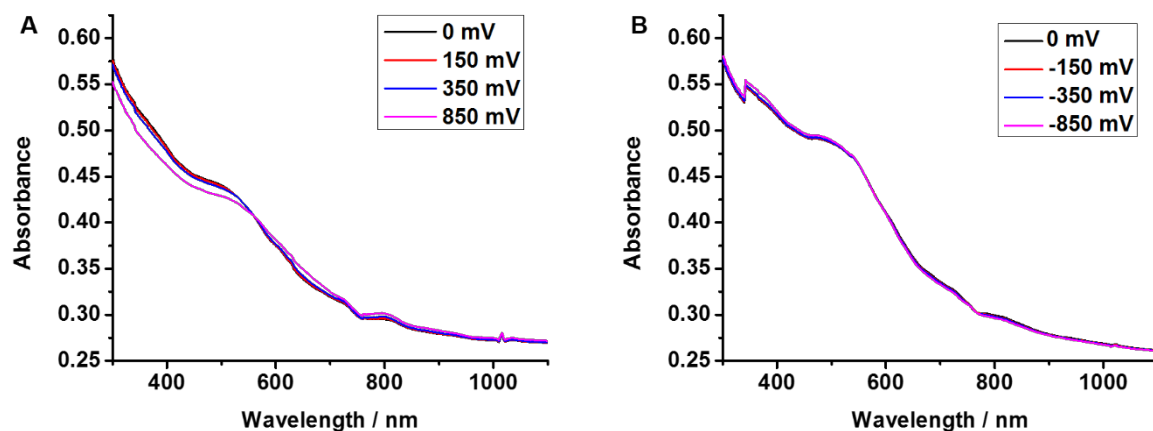
**Figure S1.** (A) DPV during oxidation of the aged Au<sub>130</sub> sample. (B) DPV during reduction of the aged Au<sub>130</sub> sample. Results measured with 0.1M TBAP as electrolyte with purging with Ar for 15-30 mins. A 0.2 mm platinum disk working electrode, platinum foil counter, and an Ag/AgCl wire were used. Low temperature measurements were done in a mixture of dry ice and ethanol (-72°C). OCP during the time of these measurements was 0.18 V



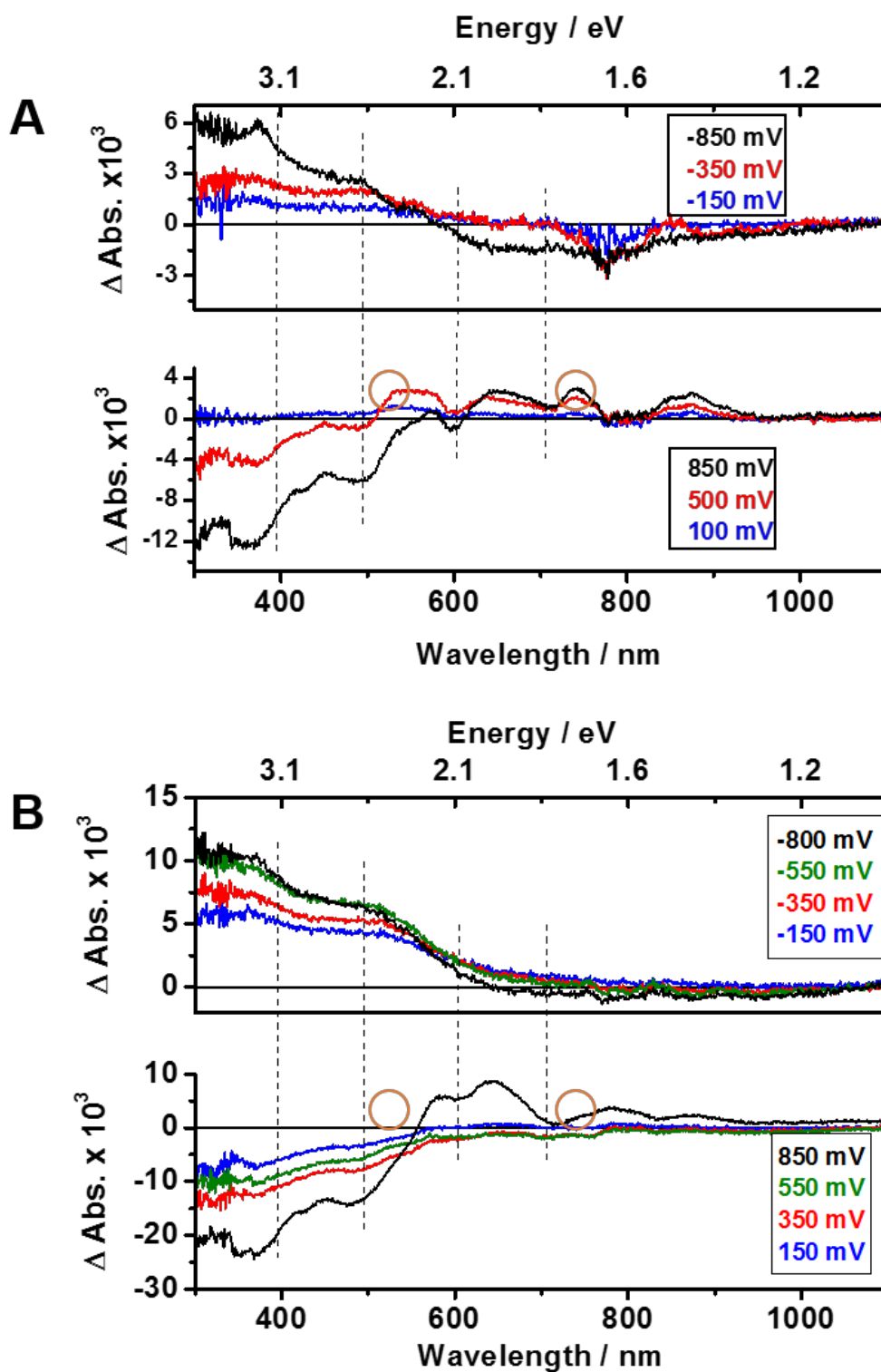
**Figure S2.** CV and DPV of Au<sub>130</sub> nanoclusters in 10:1 Toluene:Acetonitrile. (A) and (B) scan a large potential window as overview. (C) includes a less negative potential range (-0.8V) to show the largely featureless oxidation in QDL region and the reversal reduction features around +1.0V and -0.2V. Black stars in (D) highlight the 0.5 V gap consistent with the measurement in CH<sub>2</sub>Cl<sub>2</sub>. Results measured with 0.1M TBAP as electrolyte with purging with Ar for 15-30 mins. A 0.2 mm platinum disk working electrode, platinum foil counter, and an Ag/AgCl wire were used. OCP during the time of these measurements was 0.18 V.



**Figure S3.** CV (panel A) and DPV (panel B) of the 1:1 Au:p-MBT mixture in 10:1 Toluene:Acetonitrile. Results measured with 0.1M TBAP as electrolyte after purging with Ar for 15-30 mins. A 0.2 mm platinum disk working electrode, platinum foil counter, and an Ag/AgCl wire were used.

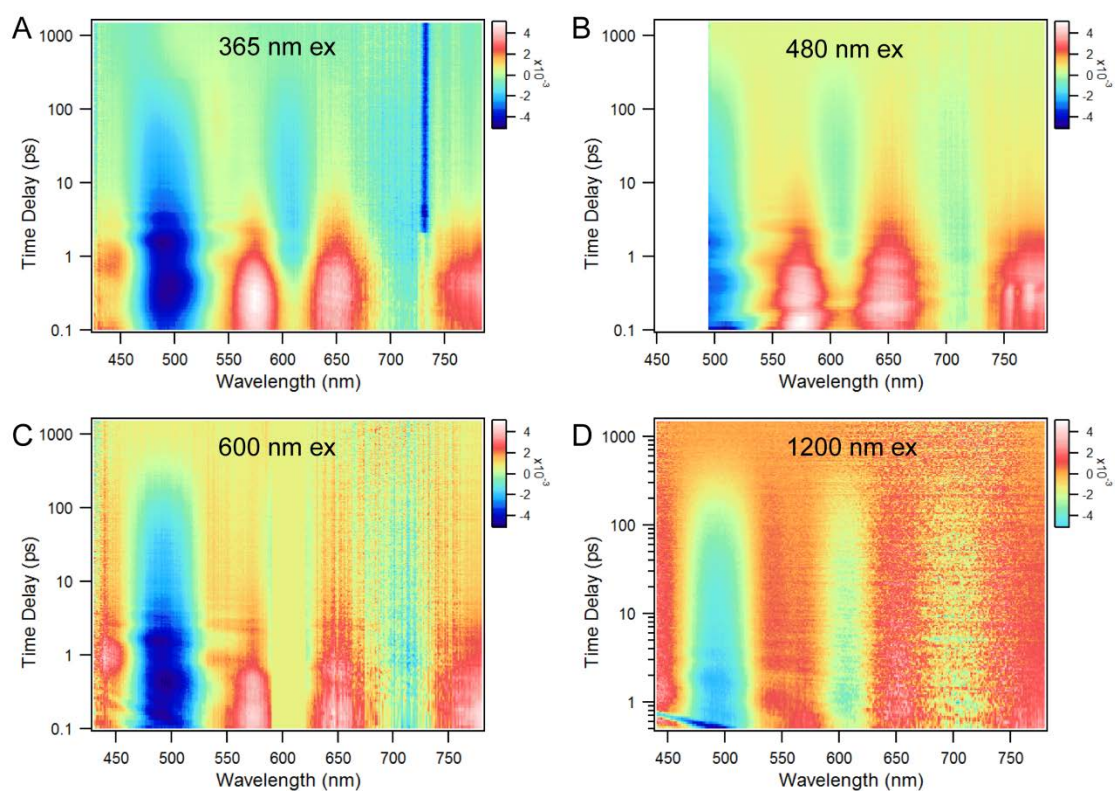


**Figure S4.** Original UV spectra measured after each electrolysis in  $\text{CH}_2\text{Cl}_2$ . A: oxidation; B: reduction. The electrolysis stopped after the charging current decrease to about less than 10% original/baseline, typically 5 minutes. These spectra were used to calculate the differential spectra shown in Figure 2 B. The abrupt change at 340 nm is an artifact due to lamp switching.

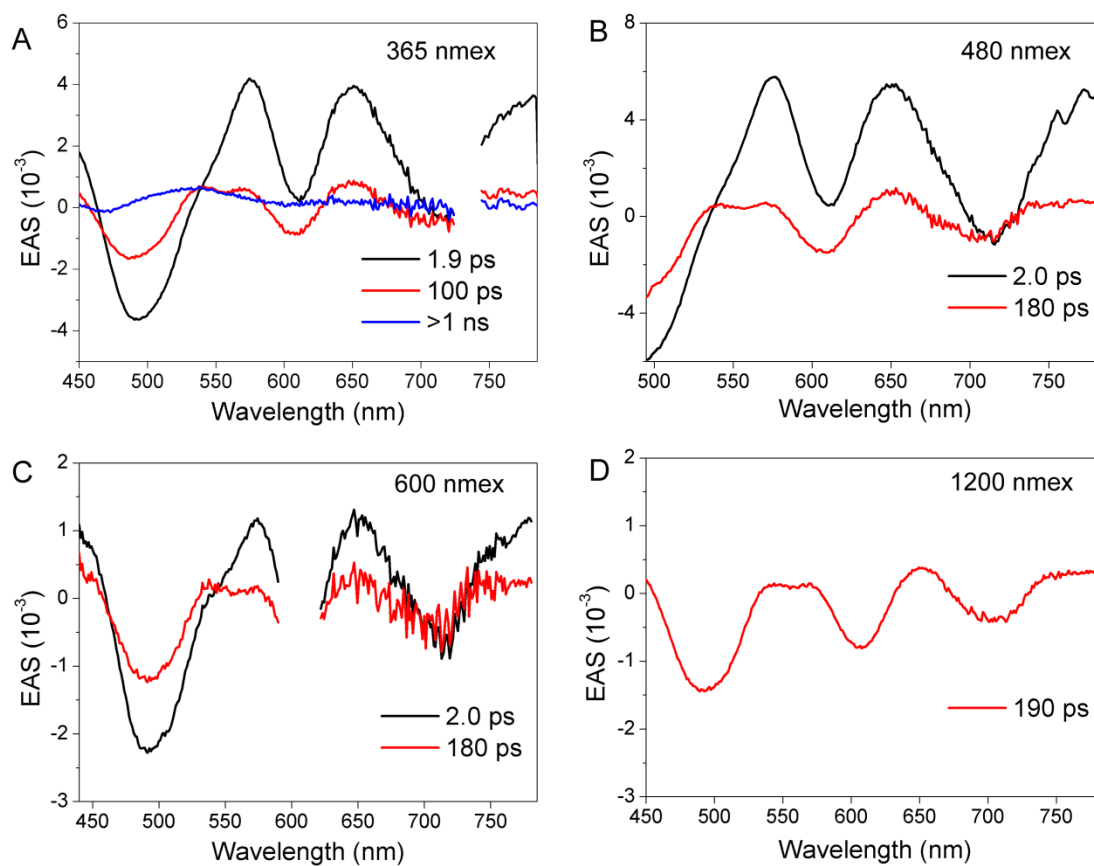


**Figure S5.** (A) Differential spectra after electrolysis in 10:1 Toluene:Acetonitrile. The OCP of the sample used in these measurements was 0.0 V. (B) Differential spectra bias after electrolysis in 10:1 Toluene:Acetonitrile. The OCP of the sample was 0.18 V (the same sample used in Figure 2). The orange circles highlight the major differences between the two samples.





**Figure S6.** Image plot of transient absorption data with optical pumping at (A) 365 nm, (B) 480 nm, (C) 600 nm and (D) 1200 nm. Residual of scattering from the pump pulse were cut off at 600 nm in C.



**Figure S7.** EAS obtained from the global analysis with excitation at (A) 365 nm, (B) 480 nm, (C) 600 nm and (D) 1200 nm.