Supporting Information

Mass Spectrometry of Small Bimetal Monolayer-Protected Clusters

Christina A. Fields-Zinna, Matthew C. Crowe, Amala Dass, Joshua E. F. Weaver and Royce W. Murray*

Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

Bruker BioTOF II Instrument Parameters:

(source is glass capillary)
Cylinder: 2500 V
End Plate: 3500 V
Capillary: 4500 V
Capillary Exit: 120 V
Skimmer 1: 40 V
Skimmer 2: 35
Offset: 15
Trap: 50
Lens: 50

Table S-1. Experimental masses and theoretical masses for PEGylated sample with extensively purified 9:1 Au:Pd mole ratio with sodium acetate, coordinating with Figure 1b in main paper. Shows mixture of $Au_{25}L_{18}$ cores and $Au_{24}PdL_{18}$ cores with various monolayers showing statistical distribution due to exchange, as well as varying numbers of Na coordinating to the PEG-thiol chain. All experimental mass values are approximately the middle of the peak; calculated mass values are found at the apex, which about the middle. Asterisks indicate peaks that are distorted enough to make this method difficult. "N/A" indicates the peak is too close to baseline for determination.

Experimental Mass	Calculated Mass	Molecular Formula
8220.59*	8220.5	[Na2Au25(SC2Ph)12(SPEG)6]3+
8243.68	8243.44	[Na3Au25(SC2Ph)12(SPEG)6]3+
8283.58	8283.30	[Na3Au24Pd(SC2Ph)11(SPEG)7]3+
8325.09*	8327.44	[NaAu25(SC2Ph)11(SPEG)7]3+
8350.98	8350.50	[Na2Au25(SC2Ph)11(SPEG)7]3+
8374.14	8373.46	[Na3Au25(SC2Ph)11(SPEG)7]3+
8414.07	8413.42	[Na3Au24Pd(SC2Ph)10(SPEG)8]3+
8456.92	8457.62	[NaAu25(SC2Ph)10(SPEG)8]3+
8481.1*	8480.52	[Na2Au25(SC2Ph)10(SPEG)8]3+
8504.18	8503.58	[Na3Au25(SC2Ph)10(SPEG)8]3+
8543.58	8543.14	[Na3Au24Pd(SC2Ph)9(SPEG)9]3+
8586.98*	8587.65	[Na1Au25(SC2Ph)9(SPEG)9]3+
N/A	8610.69	[Na2Au25(SC2Ph)9(SPEG)9]3+
8634.37	8633.53	[Na3Au25(SC2Ph)9(SPEG)9]3+
8673.76	8673.21	[Na3Au24Pd(SC2Ph)8(SPEG)10]3+
8717.4*	8717.71	[Na1Au25(SC2Ph)8(SPEG)10]3+
N/A	8740.73	[Na2Au25(SC2Ph)8(SPEG)10]3+
8764.27	8763.75	[Na3Au25(SC2Ph)8(SPEG)10]3+
8804.06	8803.7	[Na3Au24Pd(SC2Ph)7(SPEG)11]3+
N/A	8847.82	[Na1Au25(SC2Ph)7(SPEG)11]3+
N/A	8870.69	[Na2Au25(SC2Ph)7(SPEG)11]3+
8894.53*	8893.81	[Na3Au25(SC2Ph)7(SPEG)11]3+
8934.4	8933.87	[Na3Au24Pd(SC2Ph)6(SPEG)12]3+
N/A	8977.82	[NaAu25(SC2Ph)6(SPEG)12]3+

Figure Captions:

Figure S-1. Close-up view of an FT-ICR-MS spectrum of one of the species in the spectrum shown in Figure 1a, which is labeled (0,10) in Figure 1b. The spacing between the isotopic peaks is 0.33 (Panel a), dictating that the species is multiply (3+) charged, so the x-axis is multiplied by 3 to obtain Figure S-1b, showing that the molecular composition of the species is $[Na_4Au_{25}(SC_2Ph)_8(SPEG)_{10}]^{3+}$. The Au_{25} and $Au_{24}Pd$ peaks lie in the same distribution, spaced apart by the mass difference between Au and Pd, so they are equally multiply charged.

Figure S-2. OSWV voltammetry of a 0.2 mM standard purification sample made with 9:1 Au:Pd mole ratio, performed in CH_2Cl_2 with 0.1M tetrabutylammonium perchlorate. Asterisks indicate signal typical of $Au_{25}(SC_2Ph)_{18}$, while presence of other peaks indicates the presence of another species, presumably the bimetal, as the spacings between all of the peaks are irregular. Voltammetry was performed in a single compartment cell containing 0.15 cm dia. Pt disk working, Pt wire counter, and Ag/AgCl (aq) reference electrodes, under Ar.

Figure S-3. UV-vis spectrum of extensively purified 9:1 Au:Pd (red curve) sample compared to $Au_{25}(SC_2Ph)_{18}$ (black curve). The addition of Pd has smoothed out the step-like features of $Au_{25}L_{18}$ seen around 400 and 700 nm, indicating a change in optical properties for the bimetal species.

Figure S-4. Expanded view of ESI spectrum of PEGylated, standard purification sample 13:12 Au:Pd mole ratio, where simulations indicate a mixture of species. In this example, $[Na_3Au_{25}(SC_2Ph)_8(SPEG)_{10}]^{3+}$ (red curve centered at ~8765 Da) and $[Na_3Au_{24}Pd(SC_2Ph)_7(SPEG)_{11}]^{3+}$ (green curve centered at ~8804 Da) are shown, indicating the higher reactivity of the bimetal species.

Figure S-5. OSWV voltammogram of 0.2mM extensively purified 3:2 Au:Pd mole ratio sample (no PEGylation or other monolayer modification) and 0.1M tetrabutylammonium perchlorate in CH_2Cl_2. Unable to make definitive interpretations of recognizable peaks, but data shows clear change in electrochemical properties upon the addition of a single Pd atom to the Au core, as typical $Au_{25}L_{18}$ features are absent.

Figure S-6. UV-vis of extensively purified 3:2 Au:Pd mole ratio sample, with unmodified monolayer. The spectrum reveals a loss of Au_{25} features and any unique features whatsoever, indicating a drastic change in properties with the addition of Pd into the core.

Figure S-1. Close-up view of an FT-ICR-MS spectrum of one of the species in the spectrum shown in Figure 1a, which is labeled (0,10) in Figure 1b. The spacing between the isotopic peaks is 0.33 (Panel a), dictating that the species is multiply (3+) charged, so the x-axis is multiplied by 3 to obtain Figure S-1b, showing that the molecular composition of the species is $[Na_4Au_{25}(SC_2Ph)_8(SPEG)_{10}]^{3+}$. The Au_{25} and $Au_{24}Pd$ peaks lie in the same distribution, spaced apart by the mass difference between Au and Pd, so they are equally multiply charged.

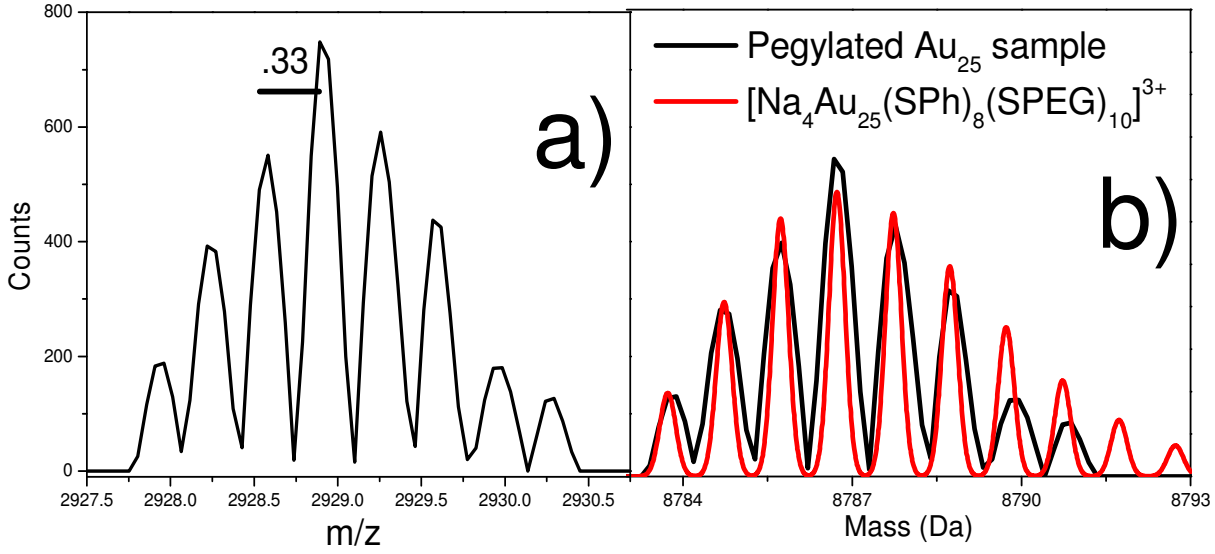

Figure S-2. OSWV voltammetry of a 0.2 mM standard purification sample made with 9:1 Au:Pd mole ratio, performed in CH_2Cl_2 with 0.1M tetrabutylammonium perchlorate. Asterisks indicate signal typical of $Au_{25}(SC_2Ph)_{18}$, while presence of other peaks indicates the presence of another species, presumably the bimetal, as the spacings between all of the peaks are irregular. Voltammetry was performed in a single compartment cell containing 0.15 cm dia. Pt disk working, Pt wire counter, and Ag/AgCl (aq) reference electrodes, under Ar.

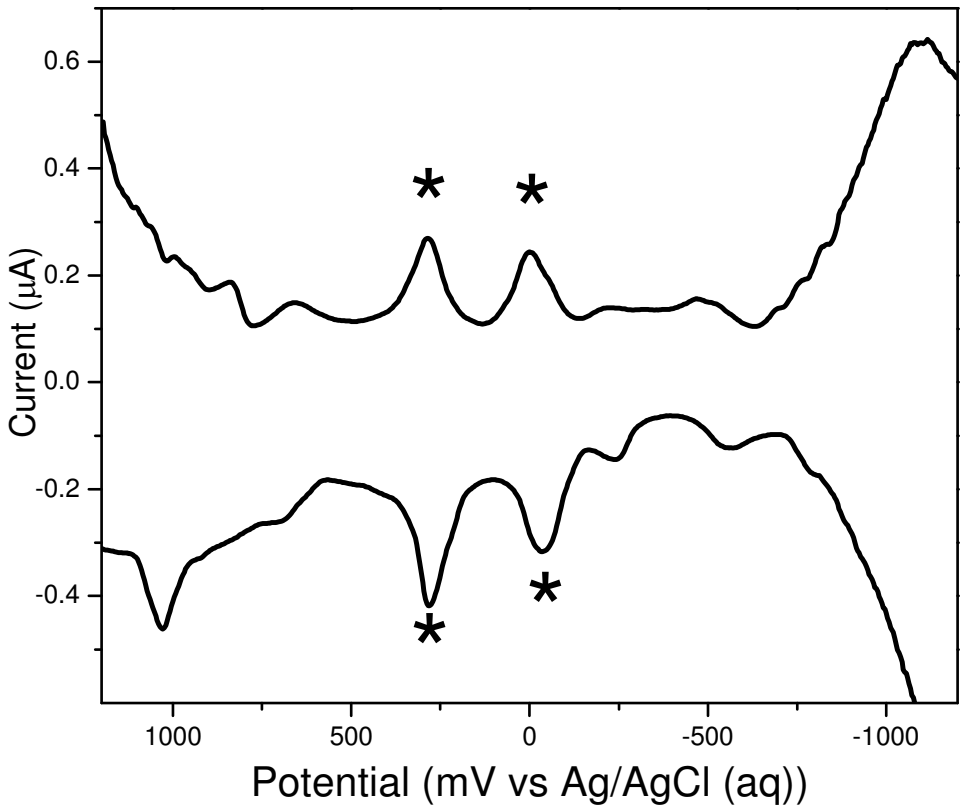

Figure S-3. UV-vis spectrum of extensively purified 9:1 Au:Pd (red curve) sample compared to $Au_{25}(SC_2Ph)_{18}$ (black curve). The addition of Pd has smoothed out the step-like features of $Au_{25}L_{18}$ seen around 400 and 700 nm, indicating a change in optical properties for the bimetal species.

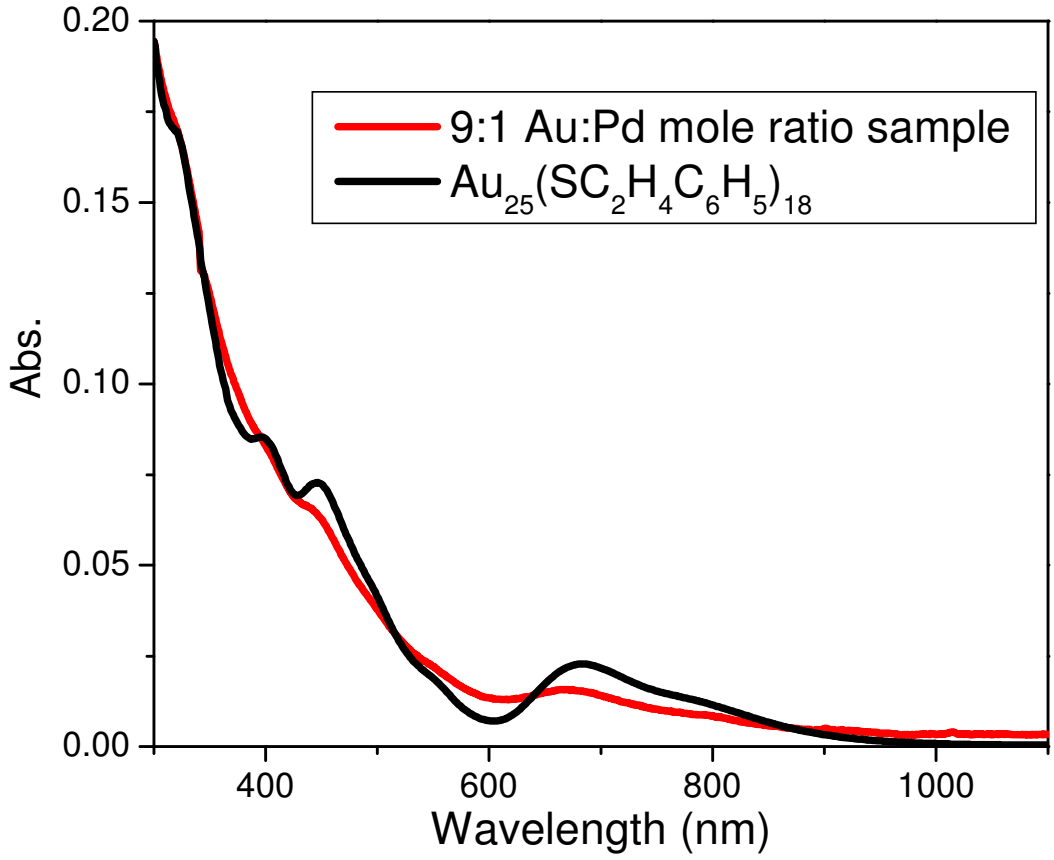

Figure S-4. Expanded view of ESI spectrum of PEGylated, standard purification sample 13:12 Au:Pd mole ratio, where simulations indicate a mixture of species. In this example, $[Na_3Au_{25}(SC_2Ph)_8(SPEG)_{10}]^{3+}$ (red curve centered at ~8765 Da) and $[Na_3Au_{24}Pd(SC_2Ph)_7(SPEG)_{11}]^{3+}$ (green curve centered at ~8804 Da) are shown, indicating the higher reactivity of the bimetal species.

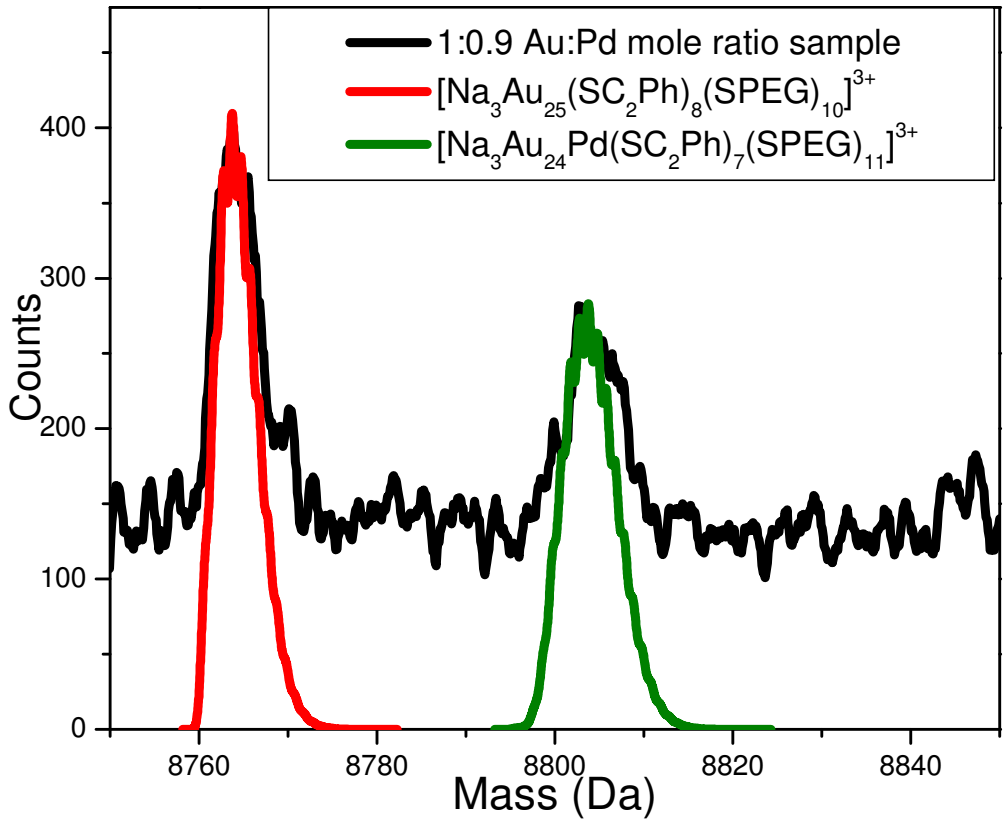

Figure S-5. OSWV voltammogram of 0.2mM extensively purified 3:2 Au:Pd mole ratio sample (no PEGylation or other monolayer modification) and 0.1M tetrabutylammonium perchlorate in CH_2Cl_2. Unable to make definitive interpretations of recognizable peaks, but data shows clear change in electrochemical properties upon the addition of a single Pd atom to the Au core, as typical $Au_{25}L_{18}$ features are absent.

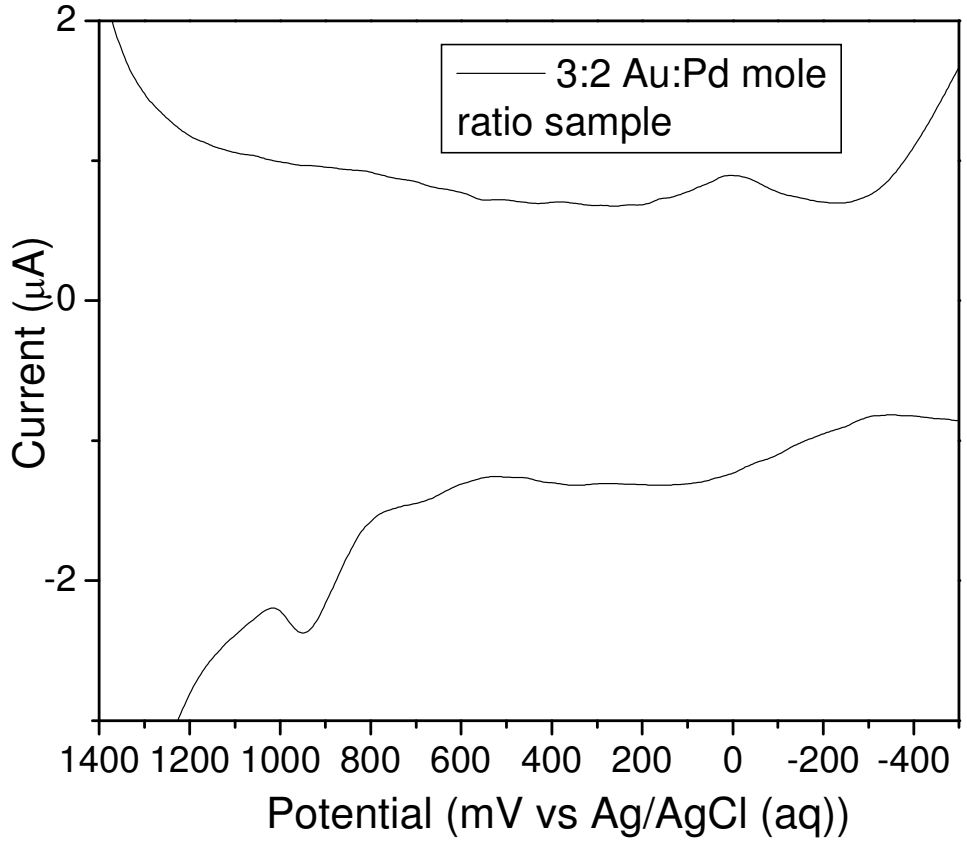

Figure S-6. UV-vis of extensively purified 3:2 Au:Pd mole ratio sample, with unmodified monolayer. The spectrum reveals a loss of Au_{25} features and any unique features whatsoever, indicating a drastic change in properties with the addition of Pd into the core.

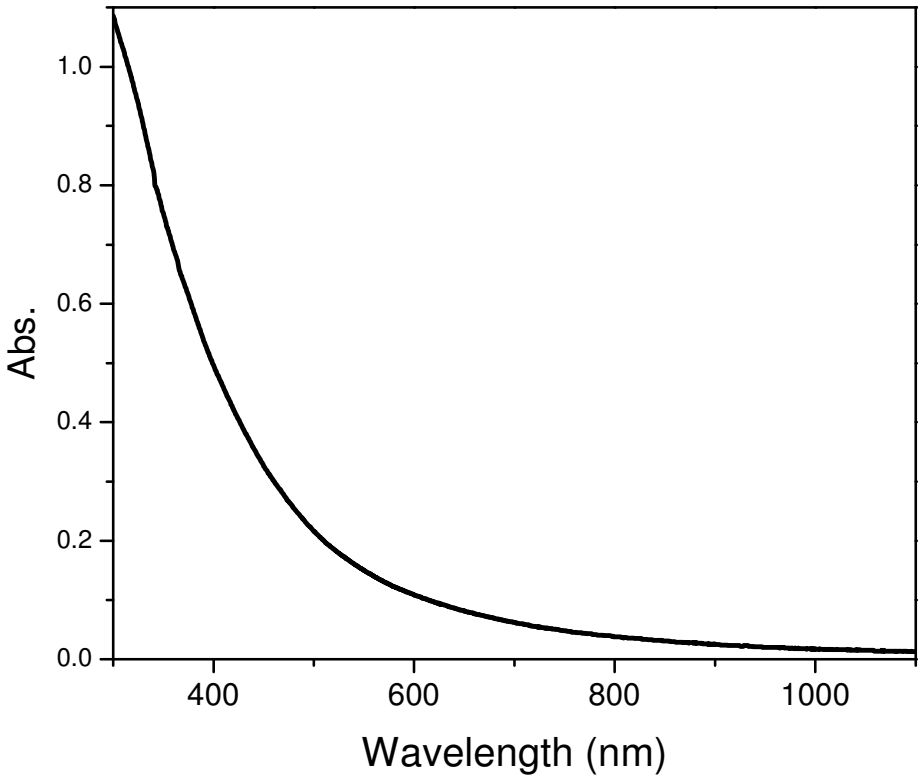

Figure S-7. ESI-QQQ spectrum of $HS(C_2H_4O)_5CH_3$ (HSPEG) in 100% methanol. Peaks include the PEGylated thiol with Na+ or Li+ coordinated to the PEG chain (NaOAc was added at a 6:1 NaOAc: HSPEG ratio and Li is residual). The peak at 303.3 m/z parallels the presence of a synthetic by-product from the manufactured starting material with olefinic functionality, as confirmed by mass spectra (not shown) of the starting material used as received by the manufacturer. There are no dimers or trimers or longer chains of HSPEG, and the ESI-TOF spectra of the 2000-4000 m/z range do not reveal any species (data not shown).