

# Supporting Information for: Self-Assembled Monolayers of Terminal Alkynes on Gold

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Experimental Procedures .....	2
Further comments on the data shown .....	3
<b>Figure S1.</b> (a) XPS survey spectrum of SAMs of decyne ( <b>1</b> , $n = 7$ ); (b) XPS Fe 2p region of SAMs of <b>3</b> ; (c) XPS F 1s and (d) C 1s region of SAMs of <b>2</b> . ....	5
<b>Figure S2.</b> Carbon (1s) region XPS spectra for SAMs of compounds <b>1</b> ( $n = 3, 5, 7, 9, 11, 13$ ), in which the signals are fit to two components assigned as C(sp) and C(sp <sup>3</sup> ). ....	5
<b>Figure S3.</b> Cyclic voltammograms at 100 mV/s of Fe(CN) <sub>6</sub> <sup>3-/4-</sup> at Au slides immersed into EtOH solutions of dodecyl alcohol (black line), dodecane (red line), dodecyl amine (green line), and dodecyne (blue line) . ....	6
<b>Figure S4.</b> CVs recorded in 0.1M NaClO <sub>4</sub> of SAMs of ethynylferrocene ( <b>3</b> ) at scan rates of 0.1-1.0 V/s (left) and 0.1-5 V/s (right). ....	7
<b>Figure S5.</b> Plot of anodic current peak intensity versus scan rates for SAMs of ethynylferrocene ( <b>3</b> ). ....	7
<b>Table S2.</b> Peak separations, surface coverages, and electron transfer rates extracted from the voltammograms in Figure S4. ....	8
<b>Figure S6.</b> CVs recorded in 0.1M NaClO <sub>4</sub> of SAMs of <b>4</b> at scan rates of 0.1-1.0 V/s (left) and 0.1-5 V/s (right). ....	9
<b>Figure S7.</b> Plot of anodic current peak intensity versus scan rates for SAMs of <b>4</b> . ....	9
<b>Table S3.</b> Peak separations, surface coverages, and electron transfer rates extracted from the voltammograms in Figure S6 .....	10
<b>Figure S8.</b> UV-Vis spectrum of dodecyne capped gold nanoparticles. ....	10
<b>Figure S9.</b> Size distribution of dodecyne-capped Au nanoparticles. ....	11

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## Experimental Procedures

**Monolayer Preparation.** Polycrystalline gold films were purchased and the gold beads were prepared by heating the gold wire ( 99.999 % ) in a natural/O<sub>2</sub> flame. The gold substrates were cleaned with “piranha” solution ( 7 : 3 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>), washed with water and ethanol followed by the sonication in ethanol for 10 min and rinsing with ethanol.

**Caution!** “piranha” solution should be handled carefully because of its violent reactivity with organic molecules. The surface areas of the gold beads were calculated from the slopes of the linear plots of the cathodic peak current obtained for the reduction of Fe(CN)<sub>6</sub><sup>3-/4-</sup> versus the square root of the scan rates. All monolayers were self-assembled by immersing the gold beads or polycrystalline gold films into 10 mM of ethanolic solutions of compounds **1-4** for 48 h. After removal from the solutions the gold slides or beads were sonicated in ethanol for 8 min and rinsed with ethanol and dried under a stream of nitrogen before characterization.

**Synthesis of Dodecyne Monolayer Protected Au Nanoparticles.** The dodecyne-capped Au nanoparticles were prepared in solution by using a modified literature method for alkylthiol-capped Au nanoparticles.<sup>1</sup> An aqueous solution (3 mL) of 0.03 M hydrogen tetrachloroaurate was mixed with 8 mL of a toluene solution containing 0.22 g of tetraammonium bromide (TOAB). After all the tetrachloroaurate was transferred into the organic layer, 14 mg of dodecyne (0.084 mmol) was added to the solution. Finally, an aqueous solution of sodium borohydride (2.5 mL, 0.4 M) was added dropwise. After further stirring for 12 h the organic layer was separated and evaporated in a rotary evaporator. Acetonitrile was added to the residue to precipitate a black solid, which was washed with acetonitrile four times to remove TOAB and unreacted dodecyne.

**Ellipsometry and Contact Angle Measurements.** Monolayer thickness was determined using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE). The He-Ne laser light was incident at 70° on the sample. All the thickness were calculated based on the refractive index of  $n_f = 1.5$ ,  $k_f = 0$ . The length of compounds **1-4** was calculated by molecular mechanics. Contact angles of water were measured shortly after removal of the gold slides from the adsorption solution. Three measurements at different spots were carried out using a model CAM 200 optical contact angle meter.

**X-ray Photoelectron Spectroscopy (XPS) Measurement.** XPS spectra were recorded on a Kratos Axis Ultra X-ray Photoemission Spectrometer using an Al  $K\alpha$  source monochromatized at 1486.6 eV. The radiations were generated at 10 mA under 15 kV. Pass energy of 160 eV and 20 eV were used for survey and regional spectrum, respectively. All spectra were referenced to the Au 4f<sub>7/2</sub> binding energy at 84 eV.

**Electrochemical Measurements.** All electrolyte solutions for electrochemical measurements were prepared with nanopure water and purged with Ar before measuring. Cyclic voltammetric measurements were conducted in a three-electrode glass cell at room temperature. A platinum wire, a Ag/AgCl aqueous solution and a monolayer modified gold slide were used as counter, reference and working electrodes, respectively. All electrode potentials are referenced to Ag/AgCl electrode. Electrochemical blocking experiments were performed with a BAS CV-50W voltammetric analyzer in a 0.1 M KCl solution containing 1 mM of Fe(CN)<sub>6</sub><sup>3-/4-</sup> redox couples. CVs of SAMs of **3** and **4** were recorded in 0.1 M NaClO<sub>4</sub>.

**Transmission Electron Microscopy (TEM).** The particle sizes and distributions were measured with a Philips CM12 TEM operated at 100kV. Images were captured using a Gatan 780 camera and DigitalMicrograph software. The samples were prepared by casting one drop of the particle in dichloromethane onto a 200-mesh carbon-coated copper grid. The particle size distribution was obtained using Scion Image Alpha 4.0.3.2 (downloaded from [www.scioncorp.com](http://www.scioncorp.com)).

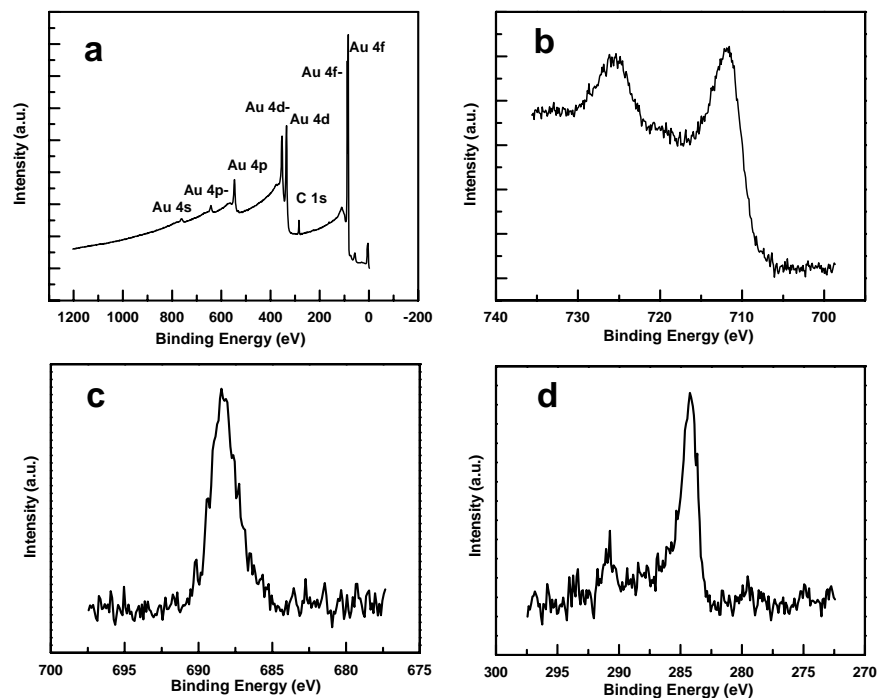
**Fourier Transform Infrared (FTIR) measurement.** FTIR measurements were carried out with a Perkin-Elmer Spectrum RX I FTIR spectrometer where the samples were prepared by compressing the materials of interest into a KBr pellet or by drop-casting a thin film of nanoparticle solutions in DCM on the NaCl disc.

### ***Further comments on the data shown***

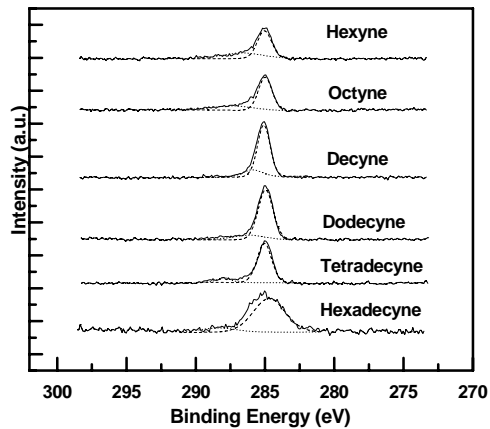
In Figure 4, the bands at 1371 and 1460 cm<sup>-1</sup> were assigned to CH<sub>3</sub> sym deformation and CH<sub>3</sub> antisym deformation, respectively. However, as an alternative assignment, the peak at 1460 cm<sup>-1</sup> might also be due to a metal-alkylidene C=C stretch. Nuckols et al.<sup>2</sup> identified a C=C stretch of a ruthenium-bound alkylidene at 1465 cm<sup>-1</sup>. However, without some type of calculation, these assignments are tenuous. Work in this area is in progress.

References:

1. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc. Chem. Commun.* **1994**, 801.
2. Tulevski, G. S.; Myers, M. B.; Hybertsen, M. S.; Steigerwald, M. L.; Nuckolls, C. *Science*, **2005**, 309(5734), 591-594



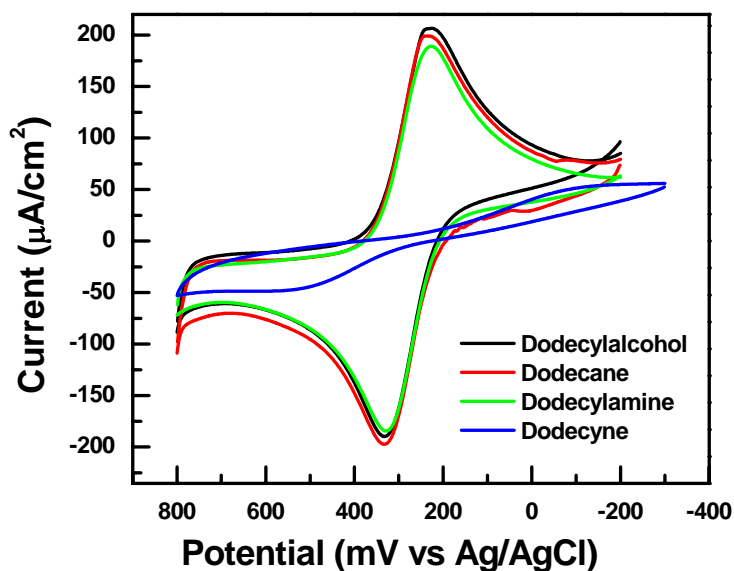
**Figure S1.** (a) XPS survey spectrum of SAMs of decyne (**1**,  $n = 7$ ); (b) XPS Fe 2p region of SAMs of **3**; (c) XPS F 1s and (d) C 1s region of SAMs of **2**.



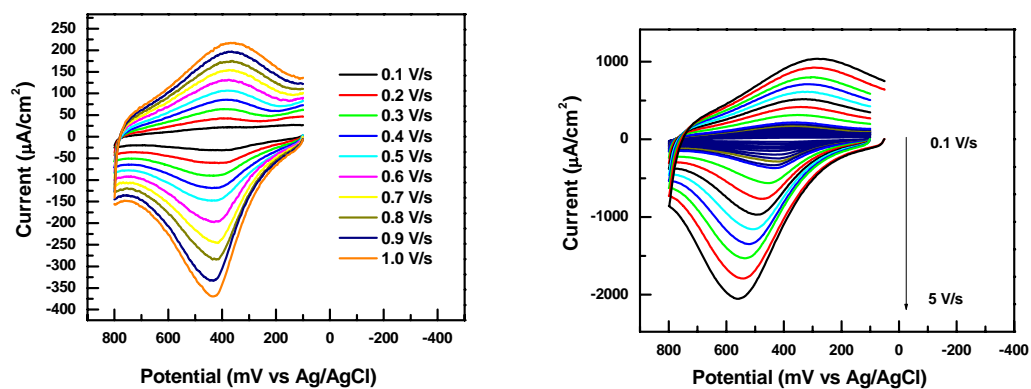
**Figure S2.** Carbon (1s) region XPS spectra for SAMs of compounds **1** ( $n = 3, 5, 7, 9, 11, 13$ ), in which the signals are fit to two components assigned as C(sp) and C(sp<sup>3</sup>).

**Table S1.** Relative areas of C1s sp (Binding Energy ca. 287 eV) and sp<sup>3</sup> (Binding Energy = ca. 285 eV) XPS signals expected and found for compounds **1** (n = 3, 5, 7, 9, 11, 13).

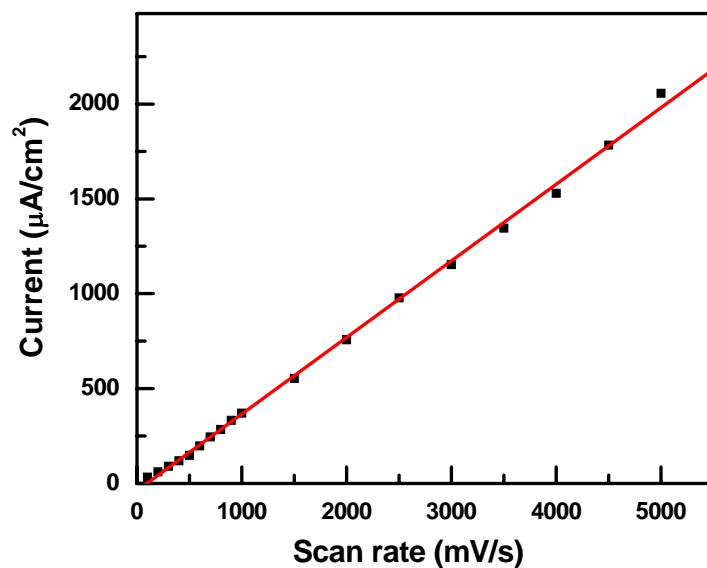
Compound	Expected percentage (%)		Measured by XPS	
	C sp <sup>3</sup>	C sp	C sp <sup>3</sup>	C sp
Hexyne	66.7	33.3	63.6	36.4
Octyne	75	25	74.5	25.5
Decyne	80	20	80.1	19.9
Dodecyne	83.3	16.7	82.7	17.3
Tetradecyne	85.7	14.3	84.6	15.5
Hexadecyne	87.5	12.5	88.2	11.8



**Figure S3.** Cyclic voltammograms at 100 mV/s of  $\text{Fe(CN)}_6^{3-/4-}$  at Au slides immersed into EtOH solutions of dodecyl alcohol (black line), dodecane (red line), dodecyl amine (green line), and dodecyne (blue line ).



**Figure S4.** CVs recorded in 0.1M NaClO<sub>4</sub> of SAMs of ethynylferrocene (**3**) at scan rates of 0.1-1.0 V/s (left) and 0.1-5 V/s (right).



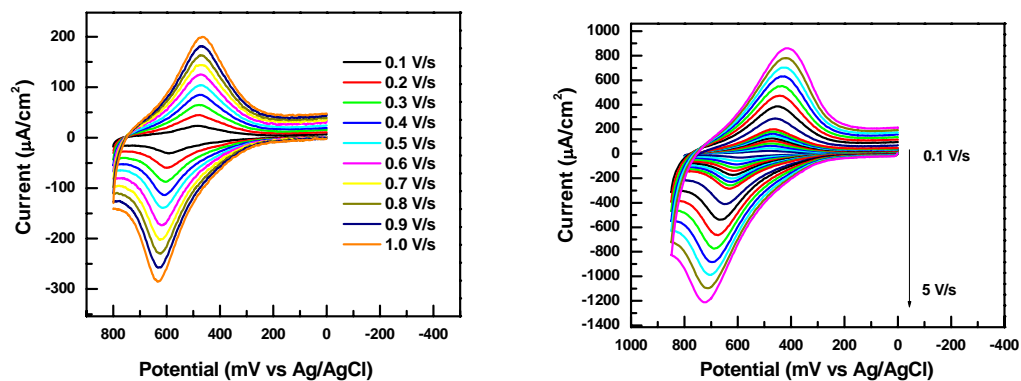
**Figure S5.** Plot of anodic current peak intensity versus scan rates for SAMs of ethynylferrocene (**3**).

**Table S2.** Peak separations, surface coverages, and electron transfer rates extracted from the voltammograms in Figure S4.

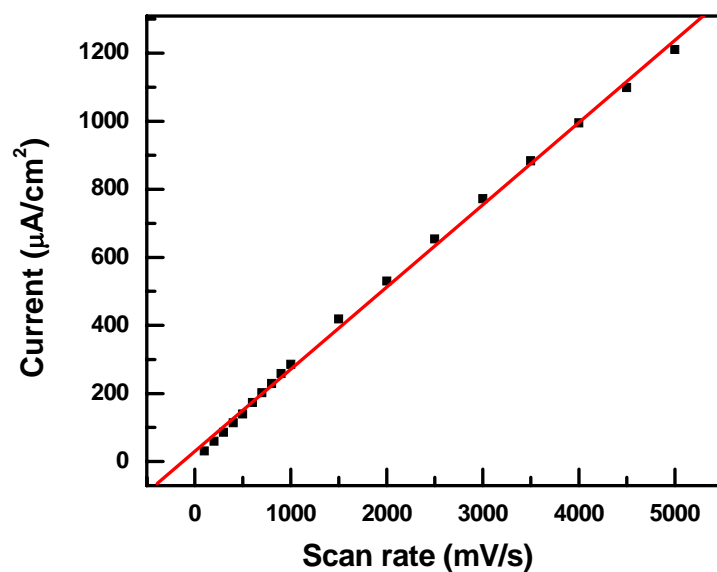
Scan rate (V/s)	$\Delta E$ (mV)	$k_{\text{ct}}$ (s <sup>-1</sup> ) <sup>a</sup>	Surface coverage (mol cm <sup>-2</sup> )	
			Anodic current	Cathodic current
0.1	13.8	10.6	3.45E-10	2.35E-10
0.2	12.6	23.2	3.25E-10	2.25E-10
0.3	23.0	18.5	3.21E-10	2.26E-10
0.4	24.0	23.5	3.17E-10	2.26E-10
0.5	28.2	24.6	3.14E-10	2.27E-10
0.6	26.8	31.2	3.50E-10	2.31E-10
0.7	30.1	32.0	3.72E-10	2.32E-10
0.8	31.2	35.1	3.78E-10	2.30E-10
0.9	49.4	22.9	3.93E-10	2.31E-10
1	51.0	24.4	3.95E-10	2.32E-10
1.5	67.7	25.4	3.93E-10	2.21E-10
2	99.3	19.8	4.03E-10	2.20E-10
2.5	126.5	16.9	4.16E-10	2.20E-10
3	143	16.6	4.09E-10	2.19E-10
3.5	171.5	13.9	4.09E-10	2.17E-10
4	191.2	12.8	4.07E-10	2.18E-10
4.5	219.6	9.8	4.22E-10	2.21E-10
5	237.9	9.1	4.38E-10	2.21E-10
Average		20.6 (3.0) <sup>b</sup>	3.78 (0.15) <sup>b</sup> E-10	2.25 (0.02) <sup>b</sup> E-10

<sup>a</sup>From a Laviron Analysis (Laviron, E. *J. Electroanal. Chem.*, **1979**, 101, 19) using a working curve provided by Professor Edmond Bowden, NCSU. <sup>b</sup>Values in parentheses represent the 90% confidence interval of values obtained.





**Figure S6.** CVs recorded in 0.1M NaClO<sub>4</sub> of SAMs of **4** at scan rates of 0.1-1.0 V/s (left) and 0.1-5 V/s (right).

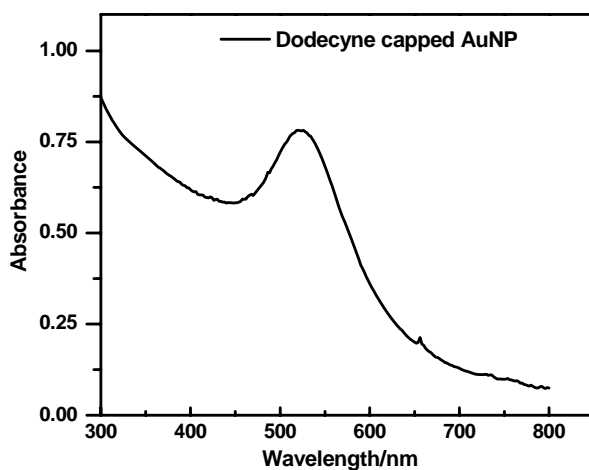


**Figure S7.** Plot of anodic current peak intensity versus scan rates for SAMs of **4**.

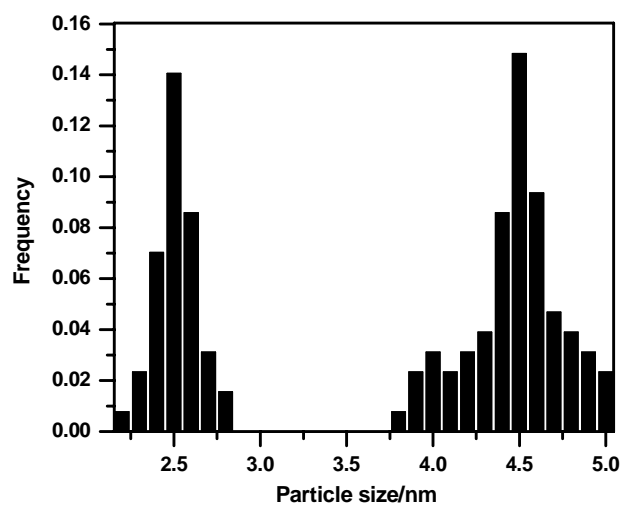
**Table S3.** Peak separations, surface coverages, and electron transfer rates extracted from the voltammograms in Figure S6

Scan rate (V/s)	$\Delta E$ (mV)	$k_{ct} (s^{-1})^a$	Surface coverage (mol cm <sup>-2</sup> )	
			Anodic current	Cathodic current
0.1	104.6	0.9	3.30E-10	2.48E-10
0.2	118.6	1.5	3.18E-10	2.38E-10
0.3	118.6	2.3	3.06E-10	2.28E-10
0.4	129.9	2.6	3.02E-10	2.23E-10
0.5	141.9	2.8	2.98E-10	2.20E-10
0.6	144.5	3.2	3.08E-10	2.22E-10
0.7	152.5	3.4	3.07E-10	2.16E-10
0.8	154.2	3.9	3.04E-10	2.18E-10
0.9	158.5	4.1	3.05E-10	2.14E-10
1	161.2	4.5	3.04E-10	2.12E-10
1.5	192.8	4.7	2.97E-10	2.03E-10
2	217.7	4.4	2.82E-10	2.03E-10
2.5	238.9	4.5	2.79E-10	2.00E-10
3	258	4.5	2.74E-10	1.99E-10
3.5	270.4	4.6	2.69E-10	1.90E-10
4	280.2	4.8	2.65E-10	1.89E-10
4.5	295.3	4.6	2.60E-10	1.87E-10
5	310.6	4.4	2.58E-10	1.85E-10
Average		3.7 (0.5) <sup>b</sup>	2.93 (0.08) <sup>b</sup> E-10	2.11 (0.07) <sup>b</sup> E-10

<sup>a</sup>From a Laviron Analysis (Laviron, E. *J. Electroanal. Chem.*, **1979**, 101, 19) using a working curve provided by Professor Edmond Bowden, NCSU. <sup>b</sup>Values in parentheses represent the 90% confidence interval of values obtained.



**Figure S8.** UV-Vis spectrum of dodecyne capped gold nanoparticles.



**Figure S9.** Size distribution of dodecyne-capped Au nanoparticles.