Supplemental Information

Synthesis of 11-mercapto-2-undecanone (1).

OH
$$\frac{PCC}{82\%}$$
 $\frac{CH_3MgBr}{94\%}$

OH $\frac{K_2Cr_2O_7}{75\%}$
 $\frac{AIBN}{thioacetic acid}$
 $\frac{A}{97\%}$

NaOMe

83%

HS

Synthesis of aminooxy terminated alkane thiolate (2).

Preparation of Gold Substrates. All gold substrates were evaporated using a Thermionics e-GUNTM evaporator. Gold substrates for electrochemical experiments were prepared by evaporating Titanium (100 Å) and then gold (1000 Å) on the silicon wafers. Gold substrates used for AFM imaging were prepared by evaporating gold (100 Å) on mica.

Preparation of SAMs. All molecules used for the preparation of SAMs were dissolved in methanol to give a final concentration of 1 mM. The gold substrates were immersed in a methanolic solution of 4 for 8 hours before being removed and rinsed with ethanol and then dried with a stream of nitrogen gas.

Electrochemical Apparatus. All electrochemical experiments were performed in 1 M HClO₄. Cyclic voltammetry was performed with a Bioanalytical Systems CV-50W potentiostat. All experiments were performed in a glass cylindrical cell with stirring of the electrolyte, and fitted with the gold substrate as the working electrode, a platinum wire as the counter electrode, and the Ag/AgCl reference electrode. All cyclic voltammograms were scanned at 100 mV/s.

Synthesis of ketone decorated gold nanoparticles. Dodecanethiol decorated gold colloids (3 mg/mL) were stirred in a solution of (1) in methylene chloride for two days at room temperature to give the desired gold nanoparticles with an average diameter of 5 nm. The resulting functionalized colloids were purified by several cycles of precipitation with hexanes, and dried under reduced pressure.

¹H NMR of 11-mercapto-2-undecanone (A) and gold colloid decorated with 11-mercapto-2-undecanone (B) in CDCl₃.

