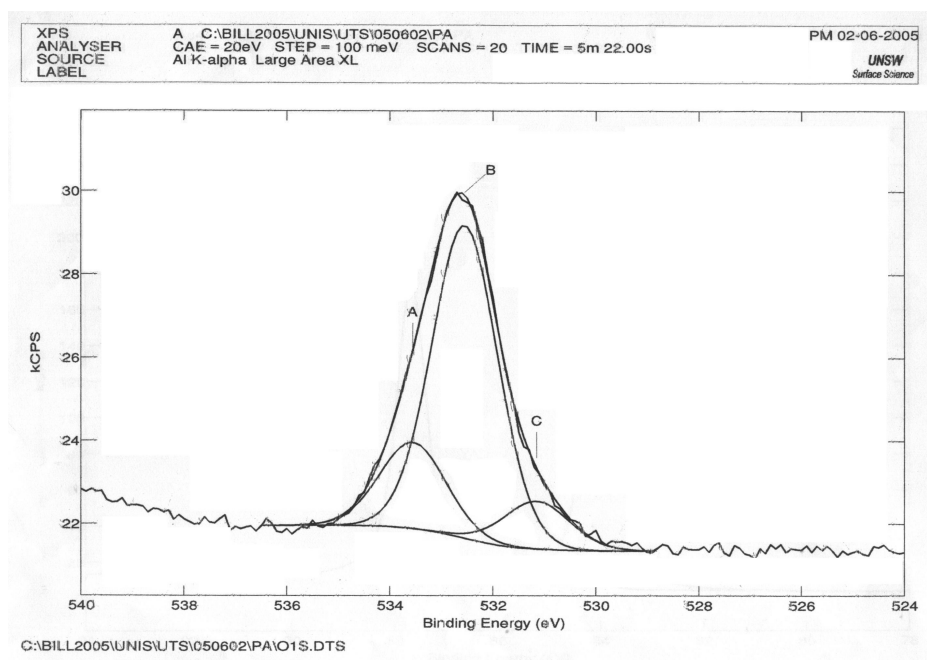# Supporting Information

Figure 1: O 1s XPS spectrum of gold(111) after immersion in ethanolic solution of ethynylbenzene and ammonium hydroxide for 24 h at 60 ℃ followed by thorough rinsing with ethanol and drying with N_2 gas.
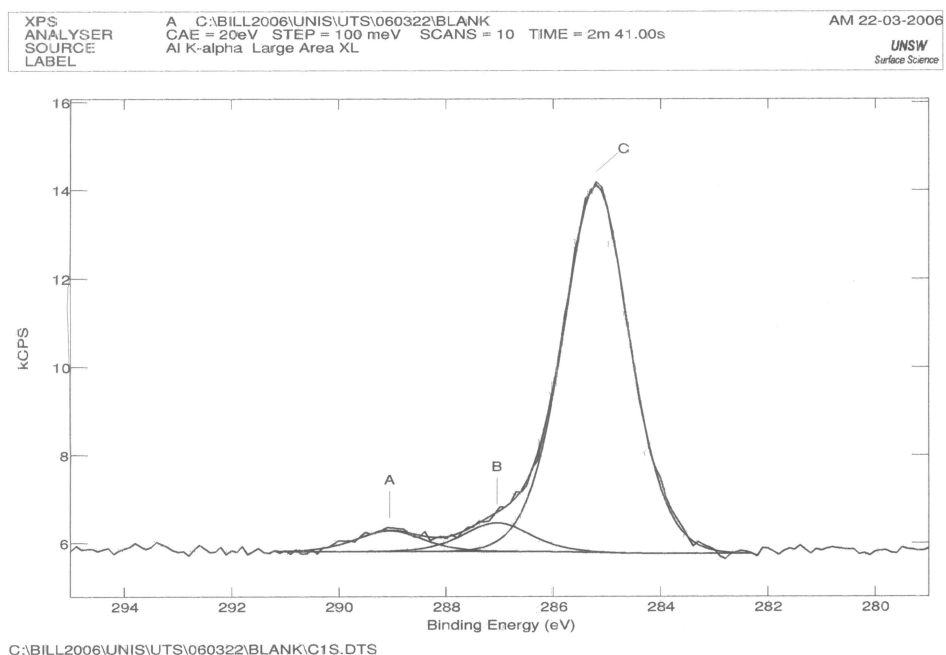
Figure 2: C 1s XPS spectrum of gold(111) after immersion in ethanol/ammonium hydroxide solution for 24 h at 60 ºC followed by thorough rinsing with ethanol and drying with N_2 gas.
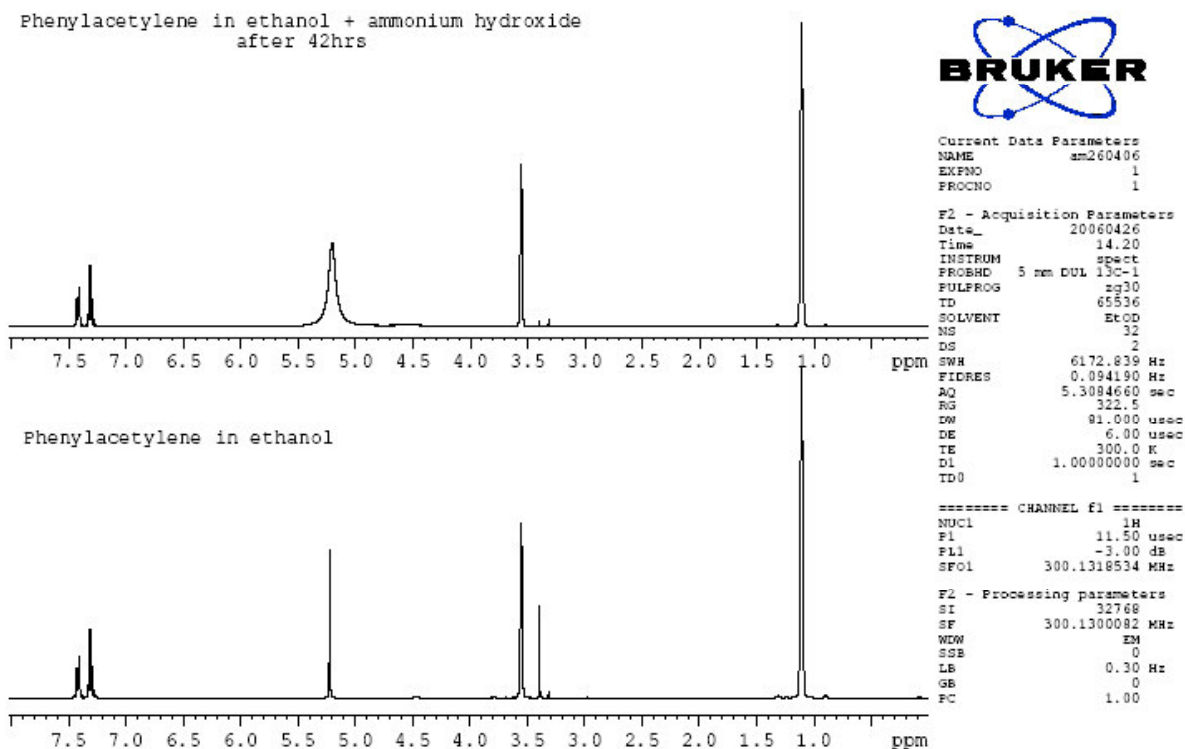
Figure 3. ^{1}H NMR spectra of ethynylbenzene in ethanol-d$_6$ before addition of ammonium hydroxide and heating (bottom spectrum), and after addition of ammonium hydroxide and heating at 60 °C for 42 h (top spectrum).
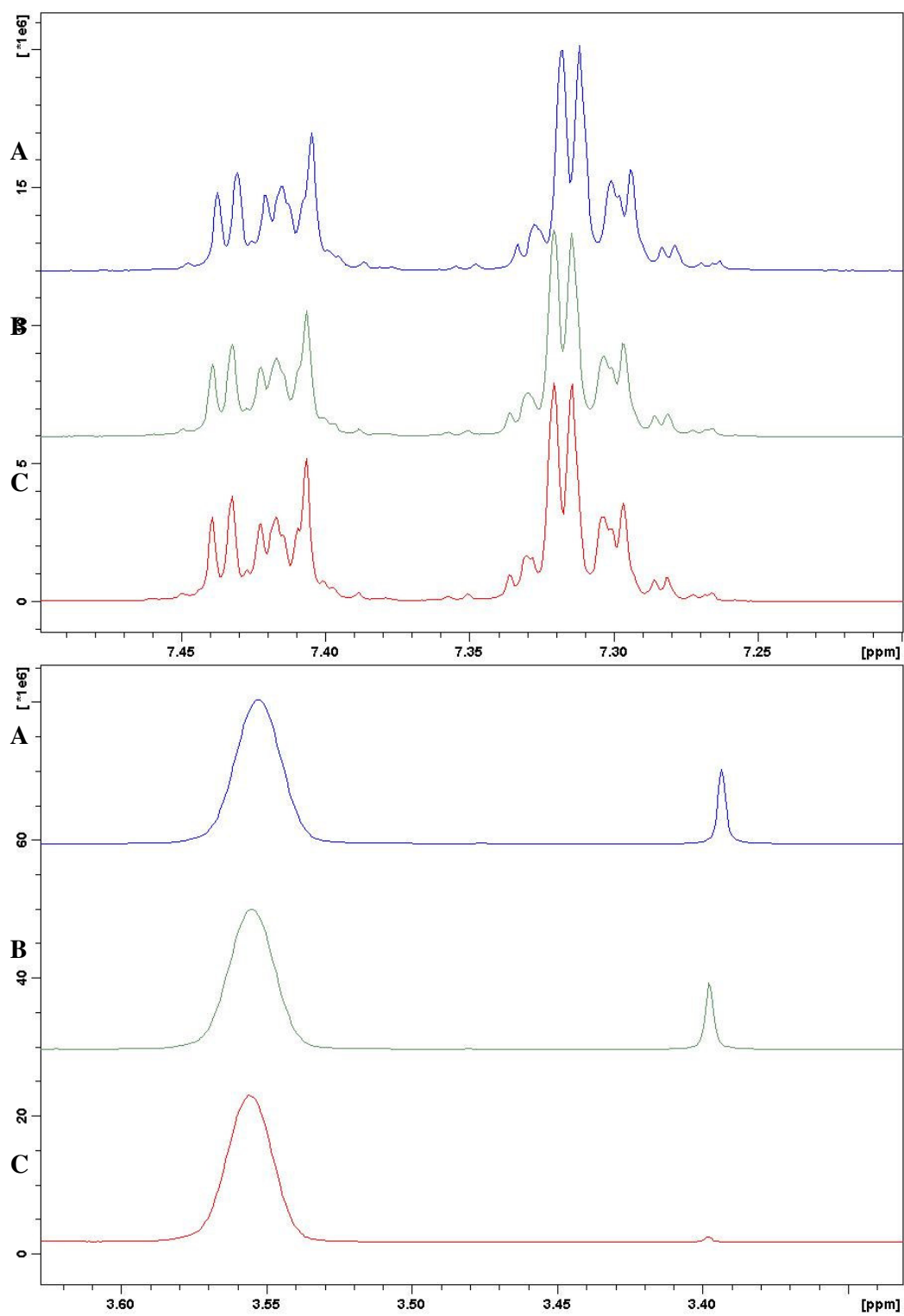
Figure 4. ^{1}H NMR spectra showing the region δ 7.20 to 7.50 (top), and δ 3.33 to 3.63 (bottom). Trace A – ethynylbenzene in ethanol-d_6 before addition of ammonium hydroxide and heating, Trace B - after addition of ammonium hydroxide but before heating, and trace C - after heating the sample at 60 °C for 42 h.
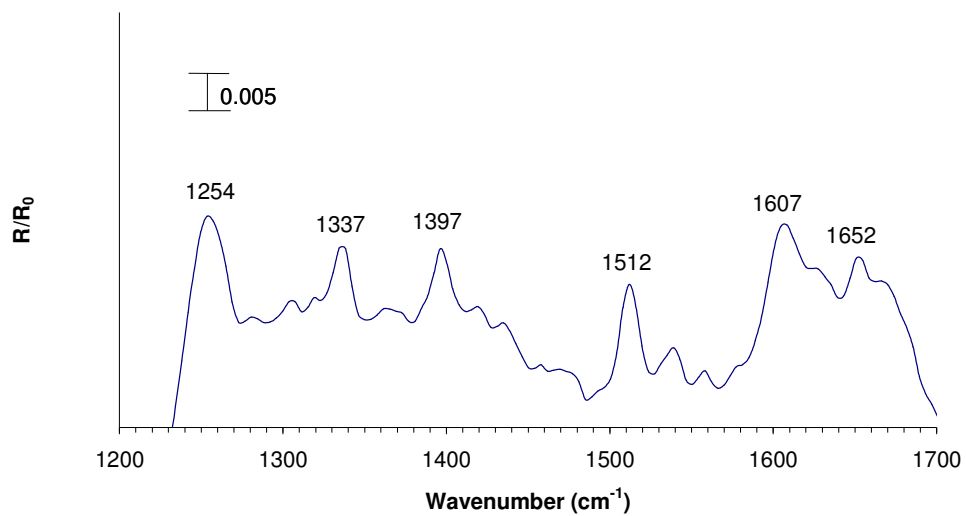
Figure 5. PM-IRRAS spectrum of a gold surface treated with a solution of ethynylbenzene in ethanol plus ammonium hydroxide.

Ellipsometry Control Experiments

Control samples, decanethiol (1 mM in ethanol) and ethanol, were incubated for 6 hours at room temperature. The samples were then washed with ethanol and dried under filtered nitrogen gas prior to measurement with ellipsometry.

Decanethiol on gold; measured 11 ± 2 Å, calculated – 12 Å

Ethanol only (no thiol); measured 0 ± 1 Å, expected 0 Å

Computational Studies. The SIESTA code[i] implements Density Functional Theory (DFT)[ii] within the linear combination of atomic orbitals (LCAO) approximation. In all calculations the generalised gradient approximation (GGA) was employed using the PBE exchange-correlation functional.[iii] All calculations are spin-restricted except for the isolated radical since only the isolated radical has an unpaired electron. The bare gold slab doe not have an unpaired electron because it periodic in two dimensions. A single, full spin-unrestricted calculation of the binding energy of phenylacetic acid was performed and yielded a result within 2 % of the unrestricted calculation.

The core electrons in Au, C, O and H were replaced by norm-conserving pseudopotentials constructed according to the scheme developed by Troullier and Martins.[iv] Relativistic corrections were used in the case of Au atoms. Cut-off radii for constructing the pseudopotentials were, for Au 2.35 a.u. for $l = 0,1$, and 1.5 a.u. for $l = 2$ and 3. For C, O and H values of 1.34, 1.15 and 1.25 a.u. respectively, were used independent of l. These pseudopotentials reliably reproduce properties for the gas phase molecule and bulk Au.[v]

SIESTA utilizes strictly localised orbitals falling to zero outside a defined cut-off radius for computational efficiency. This cut-off is defined by specifying a single energy-shift due to orbital confinement for all atoms. Care has been taken to ensure that the energy of the isolated molecule is well converged with respect to this cut-off, a value of 0.005 Ry was used throughout.[vi] In all cases double-zeta basis sets with a single polarisation function were used to represent the H 1s, C 2s, 2p and O 2s, 2p valence orbitals.

Geometry optimisations were performed using the conjugate gradient method with convergence criteria of 0.04 eV/Å.

The gold slab was constructed by first geometry optimising bulk gold then cutting a multilayer (111) slab from this bulk. Periodic boundary conditions (PBC) in SIESTA give a slab infinite in two dimensions, the required periodicity in the third dimension is taken care of by introducing a vacuum gap between these slabs. This scheme is a standard method for simulating surfaces with PBC calculations. A four-layer slab was used and the molecule adsorbed onto a 4x4 unit cell giving an inter-molecular spacing of about 4.5 A. This scheme corresponds to single molecule adsorption and results in negligible interaction between adsorbed molecules. Vacuum gaps of 30 A were employed. The use of a supercell and large vacuum gap require only a modest number of k-points to provide reasonably converged energies compared with bulk calculations. A 3x3x1 Monkhorst-Pack[vii] k-grid, giving 6 k-points in the Brillioun zone, was employed for the slab calculations and a 7x7x7 k-grid was used to optimize the bulk.

In all calculations coordinates of the gold atoms in the slab are held fixed. This is implemented primarily for computational reasons, but is justified. Relaxation of the gold (111) surface is known experimentally to be relatively small, more importantly the Au(111) surface does not substantially reconstruct. This effect is expected to be well below the level of limitations introduced by other effects such as basis set superposition errors.

The SIESTA calculations also require mesh cut-off to be specified. This parameter determines the equivalent plane-wave cut-off of the sampling grid, a value of 200 Ry was used throughout. The default convergence criteria of 10^{-4} eV for the SCF cycles was used throughout.

All atomic orbitals based methods are known to suffer from basis set superposition error (BSSE). This is a particularly important consideration where interaction energies between two constituents are being calculated. The counterpoise correction method as described by Boys and Bernardi[viii] was employed in the present work. The energies for the system as a whole, i.e. slab plus radical, and

isolated constituents, i.e. radical and slab alone, where calculated using exactly the same overall basis set with the appropriate nuclei assigned zero charge and orbitals empty. This ensures a consistent variational freedom for all calculations and is a standard method to correct for BSSE.

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