Gold Catalyzed Reduction of a Hexavalent Aromatic Sulfonyl Phthalimide to Sulfur

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I. Experimental Part

Chemicals The N-(p-flurobenzenesulfonyl)phthalimide synthesis was performed as described in the literature with minor modifications.[1] Equal molar amounts of potassium phthalimide and p-flurophenyl sulfonyl chloride were added to a round bottom flask and stirred continuously in 20-30 mL. The mixture was heated in acetonitrile under reflux for 48 hours. The product was precipitated by addition of 40-60 mL of milli-Q water, then filtered and washed well with water and left to dry. The product was then purified by recrystallization in p-xylenes.[1] N-(p-flurobenzenesulfonyl)phthalimide was obtained (93.0%).

mp 220-221 $^{\circ}$C; IR (KBr, cm^{-1}) 1801.7, 1759.4, 1588.2, 1491.1, 1383.1, 1263.0, 1224.5, 1185.9, 1154.9, 1142.2, 1088.5 and1033.8; ^{1}H-NMR (CD$_3$CN) δ (ppm): 7.34 (2H, t, J = 8.8Hz), 7.84-7.90 (4H, m), 8.16 (2H, dd, J = 5.04, 3.96 Hz) ^{13}C-NMR (CDCl$_3$) δ (ppm): 116.64, 116.86, 124.69, 130.83, 131.45, 131.55, 135.63, 162.84, 165.10 and 167.66.

Potassium phthalimide (Aldrich) and p-flurophenyl sulfonyl chloride(Aldrich) were used as received. Tetrahydrofuran, THF, (HPLC grade, Caledon Labs) was freshly distilled under argon just prior to use. Acetonitrile and Methanol, MeOH, (HPLC grade, Caledon Labs) and p-xylenes (Aldrich) were used as received.

Au(111) preparation. A gold wire (0.762 mm dia, Premion ®, 99.999%, Alfa Aesar) was evaporated onto freshly cleaved mica (V1 Grade, Ted Pella) in a custom built evaporation system, consisting of a Kurt J. Lesker bell jar, Varian turbo pump, and operating at a pressure of 1 x 10^{-7} Torr. The base plate holding the mica was heated at 600 K for 12 hours prior to depositing the gold and was kept at 600 K for an additional 3 hours after the gold was deposited to help ensure the formation of high quality Au (111) surfaces. Upon removal from the evaporation chamber, the gold samples were cleaned with Chromic Sulfuric Acid, (Chromerge ®, Bel-Art), anhydrous ethanol (Commercial Alcohols), and ultra pure water (Millipore, 18.2 MΩ) and then dried under a nitrogen stream and stored in a dessicator until used.

STM. A 5500 scanning probe microscope system (Agilent Technologies) was used for STM imaging. Images were obtained in air using a tungsten tip (0.25 mm dia, 99.95%, Alfa Aesar) electrochemically etched in 3 M NaOH (99.99%, Semiconductor Grade, Sigma Aldrich).

XPS. X-ray photoelectron spectroscopy (XPS) studies were conducted in an ultrahigh vacuum (UHV) system (Omicron) operating at a base pressure of 5×10^{-11} Torr. X-rays were generated from an Al Kα source (1486.6 eV). The system contains a hemispherical sector analyzer coupled to a multichannel electron detector. The analyzer was operated in constant analyzer energy (CAE) mode with a pass energy of 20 eV. A takeoff angle of 35° was used for all samples. All XPS spectra presented in this work are referenced to the Au $4f_{7/2}$ peak at a binding energy of 84.0 eV, and the sulfur peaks were fitted using XPSPEAK 4.1 software.

Cyclic Voltammetry. Electrochemical measurements were conducted in a three electrode glass cell thermostated at 25°C under dry nitrogen. A 2 mm diameter gold electrode (Ω Metrohm) was used. The electrode was carefully polished and ultrasonically rinsed with ethanol then electrochemically cleaned in an aqueous 0.5 M H_2SO_4 solution. The reference electrode was a saturated calomel electrode SCE. The counter electrode was a platinum wire. The electrochemical instrument used was an Autolab PGSTAT30 (Eco Chemie).

Electrolysis. Electrolysis of p-fluorophenyl sulfonyl phtahlimide was performed using a three electrode glass cell thermostated at 25°C under dry nitrogen. The Pt counter electrode was separated from the bulk solution by a glass frit. A glassy carbon plate (8 cm^2) was used as a working electrode and the reference electrode was a SCE electrode.

Theoretical calculations. The calculations were performed using the Gaussian 2003 package.[2] The full optimization was performed without imposed symmetry of the conformation using the UHF, B3LYP method with the 6-31G+(d,p) basis set starting from a preliminary optimization performed with semi-empirical methods. We checked

that the obtained conformation was real minima by running a frequency calculation for the UHF and B3LYP calculation.

1. M. S. Heller, *J. Chem. Eng. Data,* 1970, **15 (2),** 351-352.

2. Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li,; J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O.Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala,; K. Morokuma, G. A.Voth, P. Salvador,; J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. D. Farkas, K. Malick,; A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui,; A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

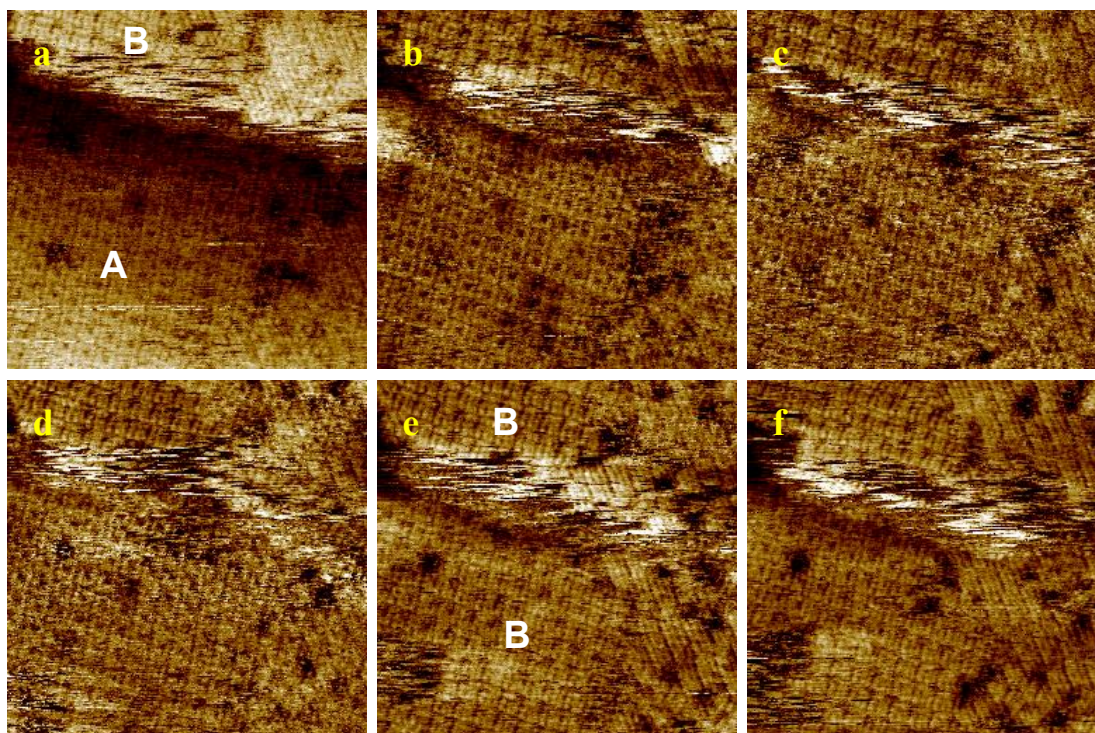## II. Observation of the A to B phase transition by STM

Figure 1. Unfiltered sequential STM images of a Au(111) surface modified using N-(p-flurobenzenesulfonyl)phthalimide (**1**) in THF/EtOH (1/1). The images are recorded using a tungsten tip, a bias voltage of 0.150 V and a tunneling current of 0.175 nA. Scan rate 4.1 ln/s.

III. Models for the phases observed by STM

As mentioned in the manuscript the rectangular structures (phase A) have been previously observed and present a good characteristic of S deposition on Au(111). An interpretation has been that these rectangular structures correspond to S octomers (S_8) adsorbed on Au (111). The proposed structure of the modified surface (C. Vericat, G. Andreasen, , M. E. Vela and R. C. Salvarezza, *J. Phys. Chem. B* 2000, 104, 302.) suggests that S atoms are deposited on hollow and top sites as per Figure 2 (this has now been added to the supporting information section). A similar rectangular structure has

also been reported for Se deposited on Au(111) providing further support for this suggestion. Assuming this structure for phase A in our STM images, the other structures correspond to structures where certain S atoms have slightly changed positions to generate different arrangements on the Au(111) surface. These new arrangements are also reported on Figure 2, showing the new positions of the S atoms on the underlying Au(111) surface. Mobility of the S atoms on the surface has been previously reported (C. Vericat, G. Andreasen, , M. E. Vela and R. C. Salvarezza, *J. Phys. Chem. B* 2000, 104, 302.). This mobility is possible also because the S-S distance (~3 Å) in these octomers is much longer than that in elemental S (~2 Å). The interaction of the S atom with the Au atom seems to weaken the S-S chemical bond allowing this mobility. Our data seem to support this mobility through observation of structures that have never been observed before and further show that these structures can be formed from the "usual" rectangular structures.

The rectangular structures have also been interpreted as a more complex AuS phase (M. M. Biener, J. Biener and C. M. Friend, *Surf. Sci.* 2007, 601, 1659). Such a rigid and complex AuS phase is incompatible with the phase changes we observed in this study. Our data provide more support for the rectangular structures being just an adsorbate S layer rather than a more complex AuS phase.
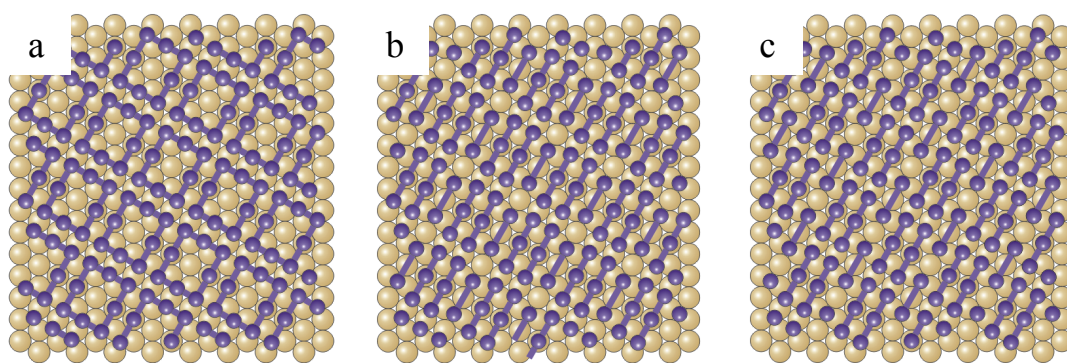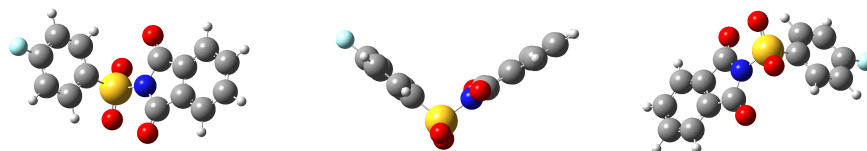

Figure 2. Proposed models for phases (a) A, (b) B and (c) C.

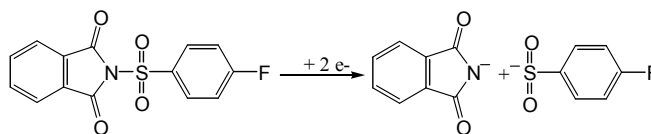## IV. N-(p-fluorobenzenesulfonyl)phthalimide optimization

Total Energy: -1391.98178767 a.u.

Scheme 1. Three different views of the optimized structure of N-(p-flurobenzenesulfonyl)phthalimide.

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	0.964255	-1.375517	0.650960
2	6	0	0.201681	-0.363823	1.242685
3	6	0	0.663601	0.952076	1.345195
4	6	0	1.923650	1.265373	0.837186
5	6	0	2.673234	0.251076	0.248543
6	6	0	2.224351	-1.062253	0.143116
7	1	0	0.578239	-2.387870	0.600153
8	1	0	0.044653	1.710326	1.811673
9	1	0	2.325527	2.270626	0.896398
10	1	0	2.853924	-1.814462	0.318789
11	16	0	-1.408846	-0.773833	1.898689
12	8	0	-1.496280	-2.212934	2.096191
13	8	0	-1.764413	0.176112	2.943006
14	9	0	3.897411	0.555289	-0.242039
15	6	0	-2.914089	0.914749	0.234942
16	6	0	-3.003495	-1.368388	-0.385514
17	6	0	-3.889874	0.754330	-0.876691
18	6	0	-3.941764	-0.590083	-1.242560
19	6	0	-4.651027	1.717045	-1.529437
20	6	0	-4.757249	-1.032353	-2.277560
21	6	0	-5.484569	1.280913	-2.567196
22	1	0	-4.598378	2.761375	-1.239923
23	6	0	-5.536655	-0.072321	-2.935687
24	1	0	-4.785329	-2.080492	-2.556553
25	1	0	-6.100011	2.000659	-3.098236
26	1	0	-6.191533	-0.377923	-3.745952
27	8	0	-2.522002	1.937097	0.749941
28	8	0	-2.712039	-2.536779	-0.468738
29	7	0	-2.475084	-0.411829	0.551148

V. Electrolysis of N-(p-fluorobenzenesulfonyl)phthalimide

Scheme 2. Global reduction reaction of N-(p-flurobenzenesulfonyl)phthalimide.

The electrolysis of N-(p-flurobenzenesulfonyl)phthalimide (**1**) was performed in acetonitrile in the presence of tetramethyl ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at its first reduction peak as determined by cyclic voltammetry. The electrolysis progress was monitored by HPLC and the products were quantified by comparison with authentic samples. The reduction consumed two electrons per molecule and provided quantitatively the phthalimide anion and the p-fluorophenyl sulfinate anion as per Scheme 2.

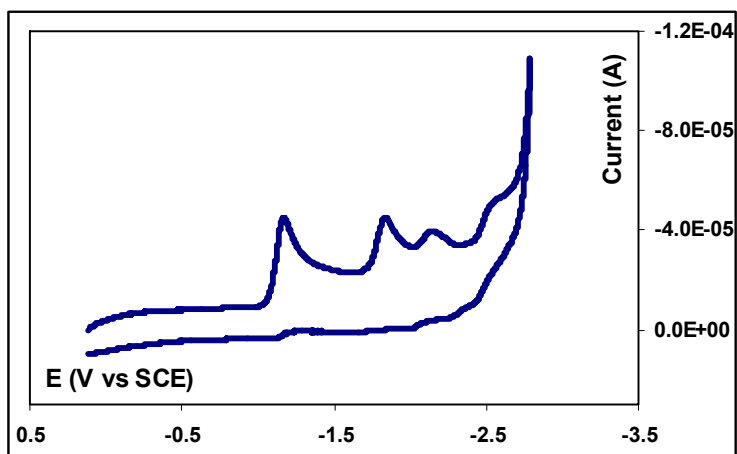## VI. Cyclic voltammetry of N-(p-fluorobenzenesulfonyl)phthalimide

Figure 3. Cyclic voltammogram at a glassy carbon electrode, in acetonitrile in the presence of 0.1 M NBu_4PF_6 (as supporting electrolyte), of N-(p-flurobenzenesulfonyl)phthalimide (1.5 mM). Scan rate v = 0.2 V/s.

The electrochemical reduction of N-(p-fluorobenzenesulfonyl)phthalimide was investigated using cyclic voltammetry (Figure 3). This study confirmed the electrolysis

results showing no total decomposition of this compound beyond the dissociation of the N-S chemical bond.

VII.   Stripping   of   Au   electrode   after   CV   scan   N-(p-fluorobenzenesulfonyl)phthalimide

Stripping experiment in a 0.5 M aqueous H_2SO_4 solution of an electrode before and after running   CV   voltammetry   scan   in   a   1   mM   solution   of   N-(p-flurobenzenesulfonyl)phthalimide in acetonitrile in the presence of 0.1 M NBu_4PF_6 as the supporting electrolyte (Figure 4) showed no difference indicating no obvious modification of the Au electrode.
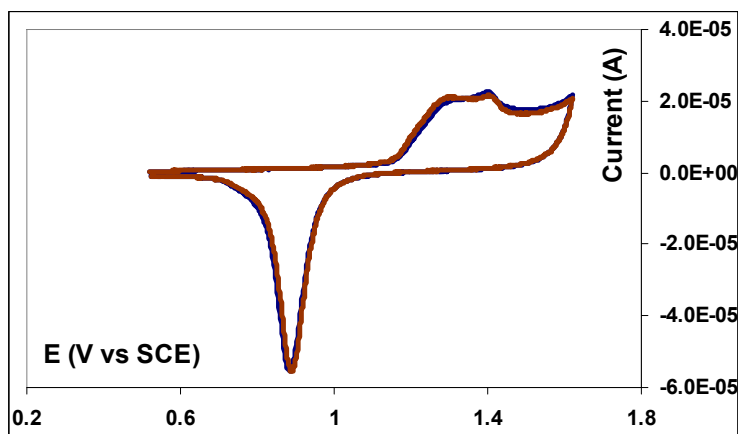

Figure 4. Cyclic voltammograms of a polycrystalline gold electrode in 0.5 M aqueous H_2SO_4 solution, before (red CV) and after (blue CV) running one CV scan in a 1 mM solution of N-(p-flurobenzenesulfonyl)phthalimide in acetonitrile in the presence of 0.1 M NBu_4PF_6 (as supporting electrolyte). Scan rate v = 0.2 V/s.