The Intriguing Reaction of Aromatic Sulfonyl Phthalimides with Gold Surfaces

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Supporting Information

I. Additional STM images of p-iodobenzenesulfonyl phthalimide modified Au(111) substrate

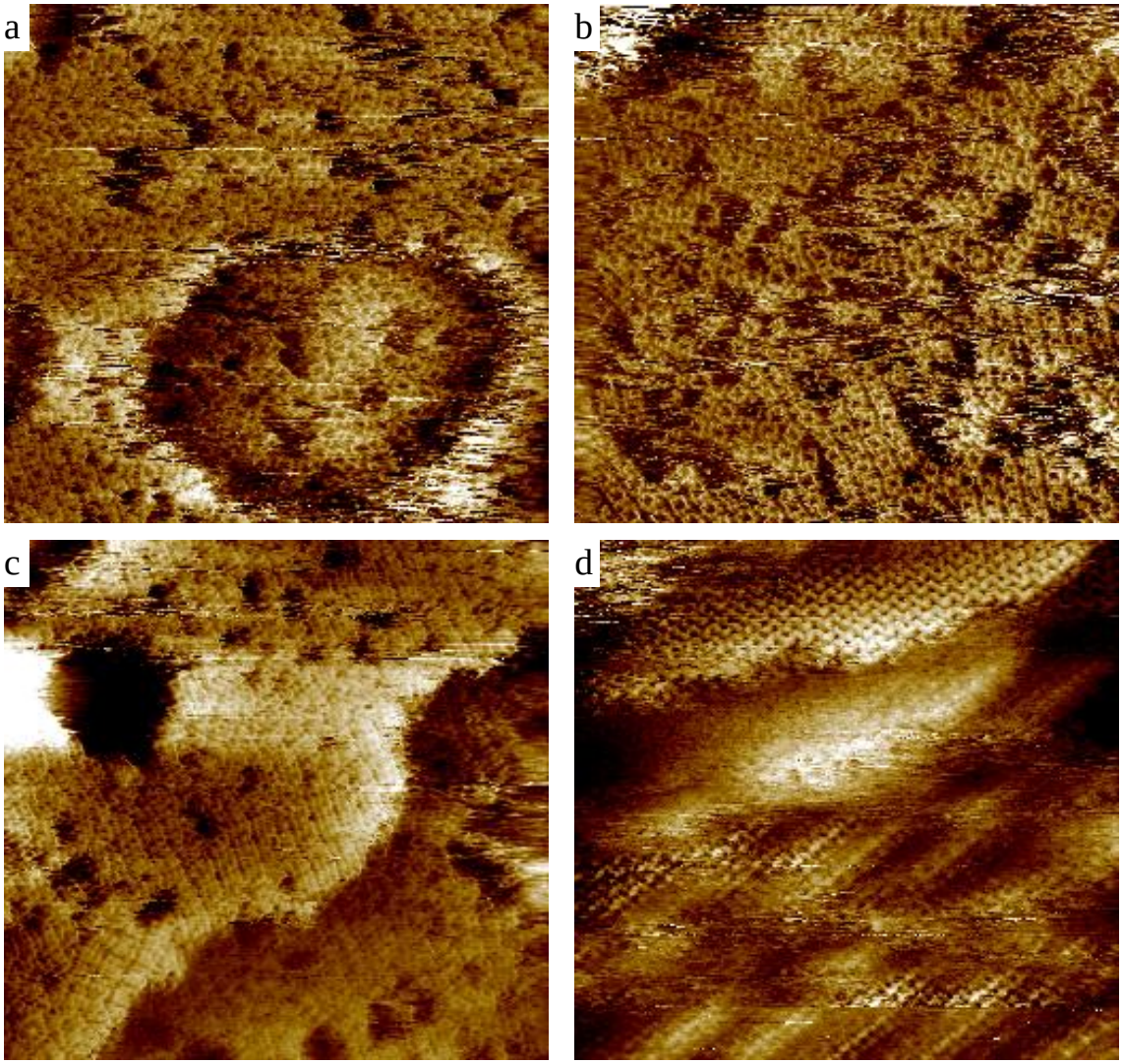

Figure S1. STM images of Au(111) modified with p-iodobenzenesulfonyl phthalimide showing different sulfur formations at scans sizes of (a) 20 x 20 nm^2, (b) 20 x 20 nm^2, (c) 18.7 x 18.7 nm^2 and (d) 20 x 20 nm^2. Imaging conditions: I = 0.4 nA and $V(Bias)$ = 0.1 V.

II. Additional STM images of p-methoxybenzenesulfonyl phthalimide modified Au(111) substrate

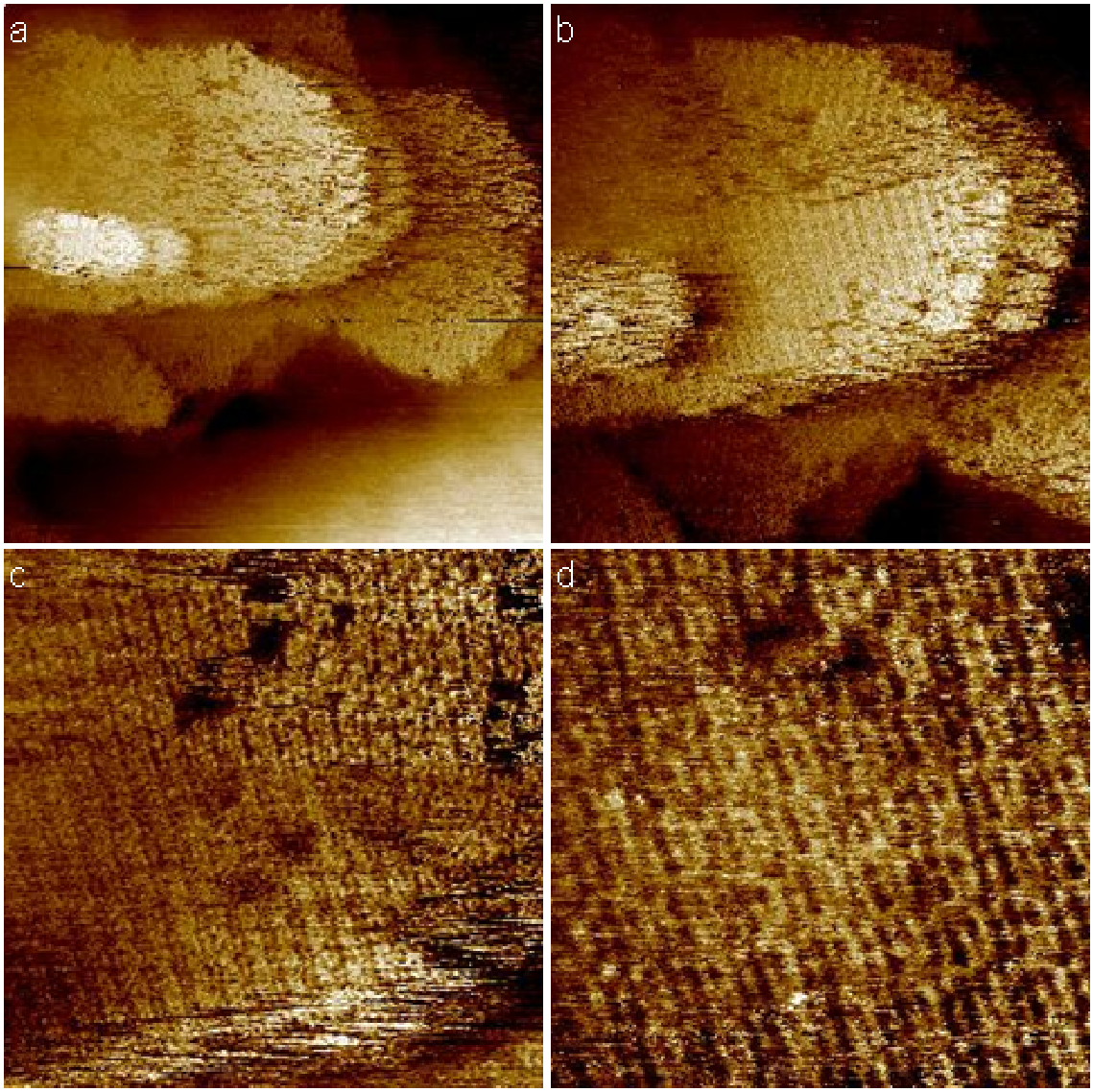

Figure S2. STM images of Au(111) modified with p-methoxybenzenesulfonyl phthalimide showing different sulfur formations at scans sizes of (a) 46 x 46 nm^2, (b) 30 x 30 nm^2, (c) 15 x 15 nm^2 and (d) 7 x 7 nm^2. Imaging conditions: I = 0.3 nA and $V(Bias)$ = 0.1 V.

III. Additional STM images of p-fluorobenzenesulfonyl phthalimide modified Au(111) substrate

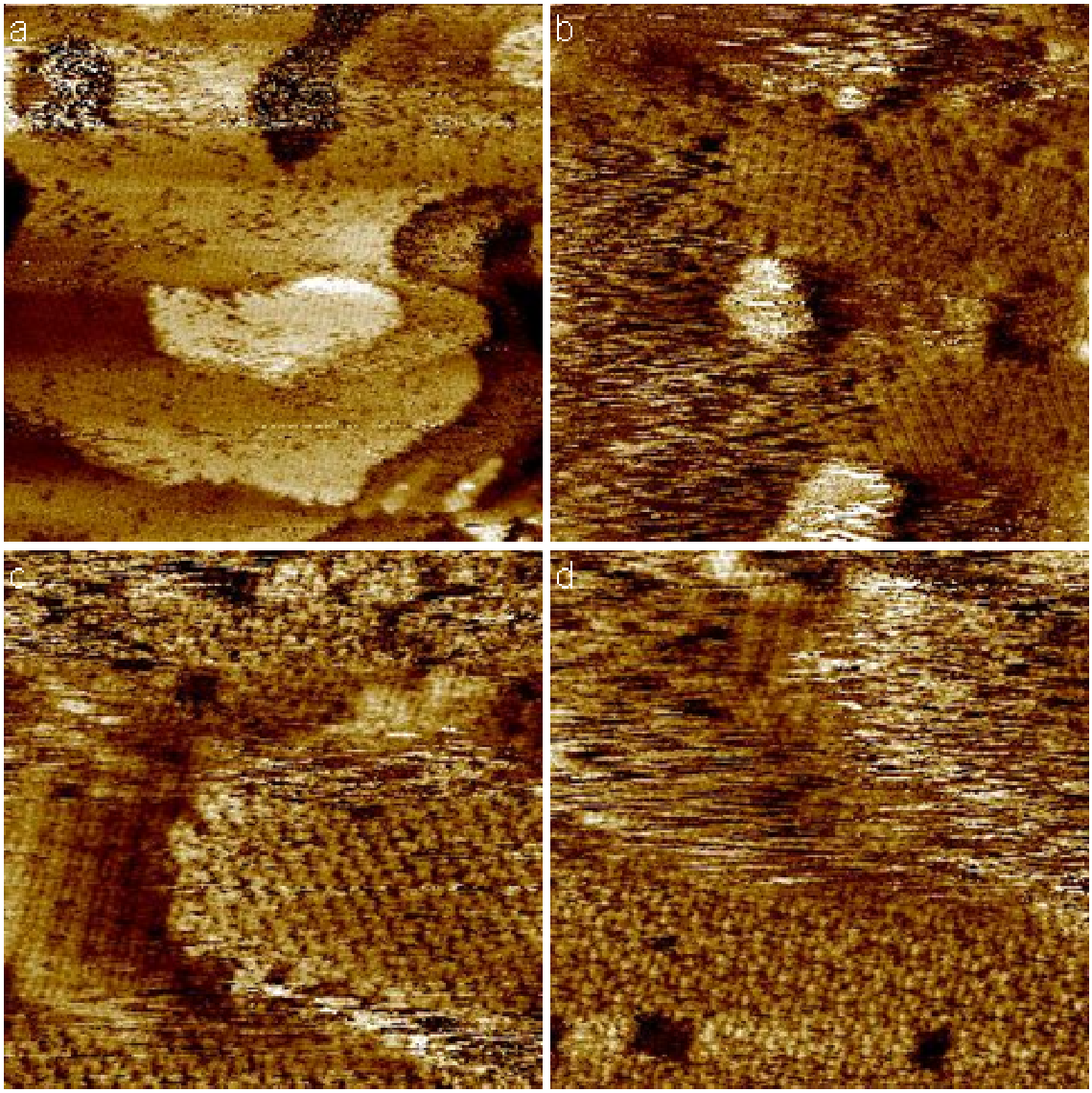

Figure S3. STM images of Au(111) modified with p-fluorobenzenesulfonyl phthalimide showing different sulfur formations at scans sizes of (a) 60 x 60 nm^2, (b) 30 x 30 nm^2, (c) 14.5 x 14.5 nm^2 and (d) 14.5 x 14.5 nm^2. Imaging conditions: I = 0.175 nA and $V(Bias)$ = 0.150 V.

IV. Models for the rectangular structures and the closely related 2:1 line pattern

Figure S4 shows the models corresponding to the rectangular structures (Figure S1) and to the closely related 2:1 line pattern (Figure S2). In the rectangular structures model the corner atoms are placed on hollow sites. Two of the edge atoms are located on hollow sites and the other two atoms on atop sites. Other models are possible. In the model for the 2:1 line pattern, sulfur atoms on atop sites have moved (to the left) to the bridge sites. The S/S are consequently afected.

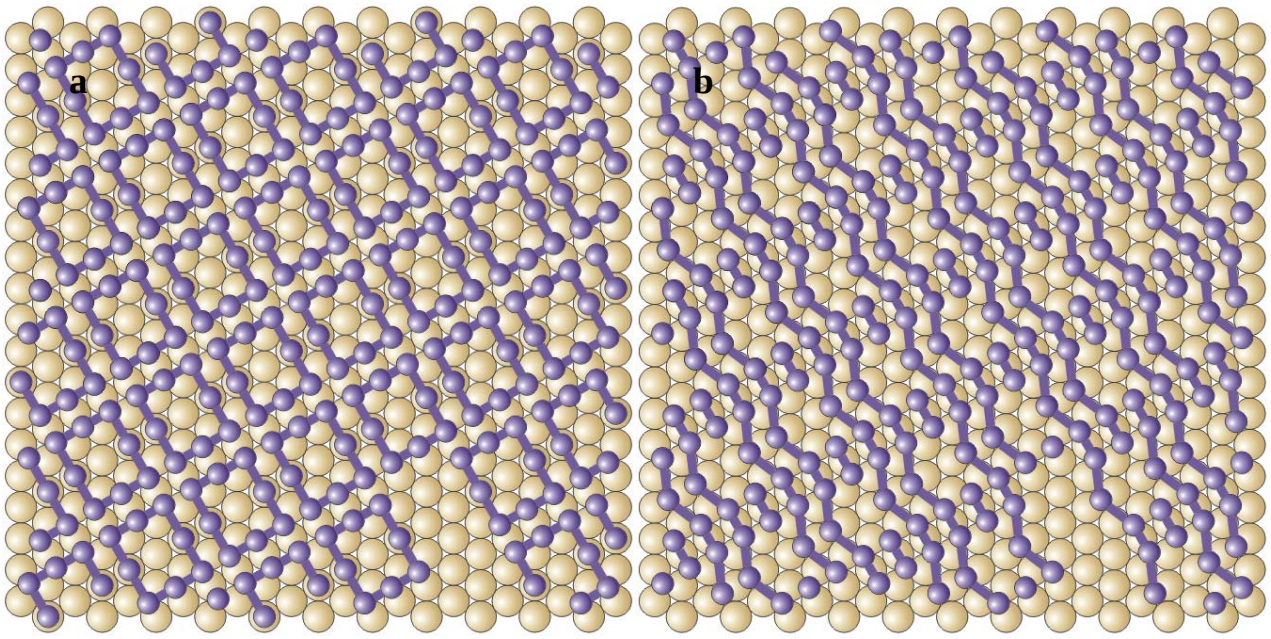

Figure S4. Proposed models for the rectangular structures (a) and for the 2:1 line pattern (b).

V. Coverage calculations from oxidative stripping cyclic voltammetry

Surface coverages were calculated assuming total conversion of sulfur to sulfate on the gold surface for gold electrodes modified with the p-methoxybenzenesulfonyl phthalimide and the p-fluorobenzenesulfonyl phthalimide. For the gold electrodes modifies with the p-iodobenzenesulfonyl phthalimide, the stripping peak includes also oxidation of adsorbed iodide. No coverage was calculated in this case. The reaction for the formation sulfate species is

$$S + 4H_2O \rightarrow SO4^{2-} + 8H^+ + 6e \quad (1)$$

which occurs simultaneously with the formation of a gold oxide monolayer

$$Au + H_2O \rightarrow AuO + 2H^+ + 2e \quad (2)$$

and/or

$$2Au + 3H_2O \rightarrow Au_2O_3 + 6H^+ + 6e \qquad (3)$$

The oxidative stripping CV were used to deduce the coverage values of the modified gold electrodes using the p-methoxybenzenesulfonyl phthalimide and the p-fluorobenzenesulfonyl phthalimide. This is readily achieved by subtracting the area under the anodic peak of the second scan, corresponding to oxidation of gold oxide, from the area under the anodic peak in the first scan, corresponding to the oxidation of the sulfur (Reaction 2) to sulfate and gold to gold oxide (Reactions 2 and 3).

VI. Theoretical calculations

The calculations were performed using the Gaussian 03 package.[1] Full optimization without imposed symmetry of the conformations were performed using the B3LYP method. The 6-31G+(d,p) basis set was used for the p-methoxybenzenesulfonyl phthalimide and p-fluorobenzenesulfonyl phthalimide the 6-31G+(d,p). The SDD basis set was used for the p-iodobenzenesulfonyl phthalimide. We checked that the conformations obtained were minima by running frequency calculations. No imaginary vibrational frequencies were observed.

Total Energies and Coordinates.

p-Iodobenzenesulfonyl phthalimide

Total Energy: -1303.21185439 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.069926	0.589373	1.383685
2	6	0	2.336176	-0.003680	1.220189
3	6	0	2.968084	0.038873	-0.038254
4	6	0	2.366495	0.676872	-1.141156
5	6	0	1.104280	1.279977	-0.987642
6	6	0	0.495684	1.206571	0.269326
7	1	0	0.555489	0.566447	2.337779
8	1	0	2.811430	-0.491341	2.064303
9	1	0	2.866384	0.714048	-2.102846
10	1	0	0.627477	1.803653	-1.810883
11	53	0	4.891076	-0.878707	-0.280996
12	16	0	-1.148553	2.078810	0.468993
13	8	0	-1.380560	2.478998	2.007077
14	8	0	-1.279737	3.176135	-0.696234
15	6	0	-3.441105	0.749069	-0.904560
16	6	0	-2.461456	-0.444375	0.914996
17	6	0	-4.226027	-0.501198	-0.645697
18	6	0	-3.648394	-1.203365	0.427097
19	6	0	-5.357751	-0.981996	-1.309274
20	6	0	-4.178201	-2.414019	0.881494
21	6	0	-5.905170	-2.204246	-0.857850
22	1	0	-5.794890	-0.431351	-2.136643
23	6	0	-5.324731	-2.909257	0.220894
24	1	0	-3.723489	-2.946726	1.711110
25	1	0	-6.787301	-2.610378	-1.345677
26	1	0	-5.770006	-3.845929	0.545422
27	8	0	-3.639638	1.608865	-1.766370
28	8	0	-1.671458	-0.728807	1.828897
29	7	0	-2.378712	0.714136	0.077123

p-Methoxybenzenesulfonyl phthalimide

Total Energy: -1407.27330966 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.174201	0.921937	-1.139344
2	6	0	1.662823	0.799921	0.160865
3	6	0	2.228869	-0.078308	1.084812
4	6	0	3.325868	-0.854859	0.709644
5	6	0	3.844434	-0.743651	-0.590269
6	6	0	3.263380	0.148341	-1.510950
7	1	0	1.725085	1.621813	-1.835860
8	1	0	1.812092	-0.155758	2.082552
9	1	0	3.763300	-1.532368	1.432290
10	1	0	3.689263	0.220970	-2.505852
11	8	0	4.905458	-1.452626	-1.053912
12	6	0	5.553557	-2.378175	-0.182987
13	1	0	6.359840	-2.818117	-0.769958
14	1	0	5.973925	-1.870641	0.693079
15	1	0	4.864101	-3.166706	0.140697
16	16	0	0.268957	1.794993	0.640418
17	8	0	0.244442	1.944976	2.089474
18	8	0	0.151864	2.935120	-0.257001
19	6	0	-1.976369	0.876134	-0.876582
20	6	0	-1.476779	-0.357611	1.077177
21	6	0	-3.023711	-0.166643	-0.673884
22	6	0	-2.729318	-0.894044	0.478021
23	6	0	-4.134614	-0.459640	-1.455987
24	6	0	-3.531872	-1.947660	0.899693
25	6	0	-4.955682	-1.514160	-1.036038
26	1	0	-4.351109	0.111006	-2.353114
27	6	0	-4.659077	-2.246742	0.123673
28	1	0	-3.290463	-2.509406	1.796092
29	1	0	-5.836236	-1.771405	-1.616915
30	1	0	-5.314953	-3.059007	0.421965
31	8	0	-0.860312	-0.779816	2.030312
32	8	0	-1.860451	1.639643	-1.804388
33	7	0	-1.105773	0.754619	0.260773

p-Fluorobenzenesulfonyl phthalimide

Total Energy: -1391.98178767 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.563059	0.501259	-1.129295
2	6	0	-2.028829	0.398514	0.158815
3	6	0	-2.456996	-0.575901	1.065818
4	6	0	-3.445707	-1.476108	0.670808
5	6	0	-3.968961	-1.365949	-0.614200
6	6	0	-3.551871	-0.398828	-1.524230
7	1	0	-2.214932	1.277912	-1.801654
8	1	0	-2.020412	-0.624670	2.057109
9	1	0	-3.811849	-2.246583	1.340027
10	1	0	-3.999823	-0.354138	-2.510577
11	16	0	-0.767771	1.560215	0.661241
12	8	0	-0.799564	2.716990	-0.221100
13	8	0	-0.776019	1.689416	2.111296
14	9	0	-4.930578	-2.238446	-0.996128
15	6	0	1.279212	-0.307358	1.116377
16	6	0	1.513039	0.894607	-0.910018
17	6	0	2.579820	-0.666351	0.489352
18	6	0	2.716984	0.040870	-0.704391
19	6	0	3.551508	-1.561349	0.921849
20	6	0	3.832077	-0.114950	-1.519333
21	6	0	4.684644	-1.718330	0.113574
22	1	0	3.431545	-2.110568	1.849849
23	6	0	4.822650	-1.006654	-1.088181
24	1	0	3.925234	0.437177	-2.448687
25	1	0	5.469688	-2.403311	0.419046
26	1	0	5.712241	-1.152420	-1.693299
27	8	0	0.761491	-0.784545	2.100454
28	8	0	1.234575	1.572897	-1.868868
29	7	0	0.716703	0.705754	0.273935