

Electrostatic Surface Potentials of Self-Assembled Monolayers of Aromatic Dithiols are tuned by Molecular Conformations

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ABSTRACT:

Density Functional Theory (DFT) calculations are performed on benzylmercaptan ($C_6H_5-CH_2-SH$), xylyldithiol ($HS-CH_2-C_6H_4-CH_2-SH$), pentamethylbenzylmercaptan ($C_6(CH_3)_5-CH_2-SH$), and tetramethylxylyldithiol ($HS-CH_2-C_6(CH_3)_4-CH_2-SH$), each adsorbed on a cluster of four gold atoms representing the hcp site on the Au(111) surface. The dipole moments of the adsorbed molecules are examined and related to the experimentally measured electrostatic surface potentials developed by self-assembled monolayers of these molecules. Four conformers of each of the dithiols are examined. The calculations indicate, contrary to the generally accepted model, that the Au-S bond dipole makes a negligible contribution to the surface electrostatic force. This results in a significant conformational dependence of the electrostatic surface potential, and it is suggested that the dithiols preferentially form SAMs in which the molecules are present in one particular conformer.

INTRODUCTION

The electrostatic surface potential (ESP) developed by a self-assembled monolayer (SAM)[1] on a metal is one of the main determinants of its electrical properties and charge transfer characteristics that modulate band alignments. The potentials are highly sensitive to the structure, orientation, and nature of the bonding between adsorbed molecule and the surface. The ESP of a SAM, relative to that of the bare surface, is given by[3]

$$V_{surf} = \frac{N_{mol}}{2K\epsilon_0} \frac{\sum \vec{m}}{m} \quad (1)$$

where N_{mol} is the local density of molecules in the SAM, \vec{m} is the dipole moment of the adsorbed molecule is a unit vector normal to the surface, K is the relative dielectric constant of the molecular monolayer, and ϵ_0 is the permittivity of vacuum. In contrast to the detailed knowledge available for current-voltage characteristics, measurements of the ESPs of SAMs have only recently become possible through advances in conducting probe technology[4]. This Communication reports that the experimentally observed contrast between the ESPs of certain aromatic monothiols and dithiols can be traced to a sensitive dependence of the ESPs of the dithiol SAMs on molecular conformation.

Howell et al. have reported measurements of the ESPs of monolayers of benzylmercaptan (BM; $C_6H_5-CH_2-SH$), xylyldithiol (XYL; $HS-CH_2-C_6H_4-CH_2-SH$), pentamethyl-benzylmercaptan (PMBM; $C_6(CH_3)_5-CH_2-SH$), and tetramethyl-xylyldithiol (TMXYL; $HS-CH_2-C_6(CH_3)_4-CH_2-SH$) on Au (111), using scanning probe microscopy methods. They noted that the ESPs of the monothiols BM and PMBM were appreciable (~ 200 mV, allowing for experimental error) whereas those of the dithiols XYL and TMXYL were smaller by a factor of three or more. Based on Eq. (1), this would mean that the dipole vectors of monothiols adsorbed on Au surfaces have significantly larger surface-normal components \square_z than the dithiols[6]. Since it is commonly assumed that the H atom of the S-H group of thiols is lost when they form SAMs (as opposed to single molecules adsorbed on gold), the general interpretation of these observations has been that the Au^+-S^- dipole is comparable in magnitude to the terminal H^+-S^- dipole and gets cancelled in dithiols due to molecular symmetry. However, preliminary DFT calculations failed to lend support to these assumptions and, in fact, yielded comparable dipole moments for both mono and dithiols. Here we report further DFT studies undertaken to examine these systems in more detail in order to develop a deeper understanding of the charge distributions in the adsorbed molecules.

Monolayers of Aromatic Dithiols are tuned by Molecular Conformations

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Computer science, Louisiana Tech University, Ruston, LA 71272*

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-CH

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-SH), xylyldithiol

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-C

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-SH), pentamethylbenzylmercaptan (C

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-SH), and tetramethylxylyldithiol (HS-CH

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-C

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-SH), each adsorbed on a cluster of four gold atoms representing the hcp site on the Au(111) surface. The dipole moments of the adsorbed molecules are examined and related to the experimentally measured electrostatic surface potentials developed by self-assembled monolayers of these molecules. Four conformers of each of the dithiols are examined. The calculations indicate, contrary to the generally accepted model, that the Au-S bond dipole makes a negligible contribution to the surface electrostatic force. This results in a significant conformational dependence of the electrostatic surface potential, and it is suggested that the dithiols preferentially form SAMs in which the molecules are present in one particular conformer.

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SAM

mol

0

ur

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\$

(1)

where N

mol

V =

2 N

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is the local density of molecules in the SAM, m ur

is the dipole moment of the

adsorbed molecule is a unit vector normal to the surface, K is the relative dielectric constant of the molecular monolayer, and

is 0

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(BM; C

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-SH), and tetramethyl-xylyldithiol (TMXYL; HS-CH

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than the dithiols[6]. Since it is commonly assumed that the H atom of the S-H group of thiols is lost when they form SAMs (as opposed to single molecules adsorbed on gold), the general interpretation of these observations has been that the Au⁺-S⁻ dipole is comparable in magnitude to the terminal H⁺-S⁻ dipole and gets cancelled in dithiols due to molecular symmetry. However, preliminary DFT calculations failed to lend support to these assumptions and, in fact, yielded comparable dipole moments for both mono and dithiols. Here we report further DFT studies undertaken to examine these systems in more detail in order to develop a deeper understanding of the charge distributions in the adsorbed molecules.

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RESULTS

Note, from Eq. (1), that only the μ_z component of the dipole vector is relevant for the magnitude of V_{SAM} . In order to compare the dipole vectors of the molecules, we transformed to a coordinate system in which the Z-axis coincided with the Au_4 -S direction. Table 1 shows that the μ_z of BM and PMBM are 2.2-3.2 D, whereas those of XYL and TMXYL range, depending on molecular conformation, from comparable values to those smaller by a factor of 4 or more.

Table 1. Dipole moments (in Debye) of the molecules studied.

Molecule	μ_x	μ_y	μ_z	$ \mu $	
BM	-1.35	0.20	2.20	2.59	
PMBM	0.34	-0.34	3.24	3.28	
XYL	(a)	1.88	-0.09	1.71	2.54
	(b)	1.79	-1.52	3.09	3.88
	(c)	-0.99	-0.84	1.17	1.75
	(d)	0.47	-1.59	0.27	1.68
TMXYL	(a)	2.00	0.63	1.34	2.49
	(b)	2.13	0.12	3.02	3.69
	(c)	-0.96	-0.14	1.58	1.85
	(d)	0.29	0.59	0.52	0.84

In order to understand the trends in the dipole moments reported in Table 1, it is useful to examine the charge distributions in the molecules. Mulliken charge distributions, which are obtained from a somewhat arbitrary partitioning of the density matrix among the atoms, tend to assign partial positive charges to the S atoms in these molecules[7], counter to experimentally established trends in electro negativities. However, the use of B3LYP electrostatic fitting charges is well-validated in previous work. We, therefore, base our conclusions on CHelpG.

Table 2. CHelpG charge distributions for the molecules studied.

Molecule	Au ₄	S (bottom)	CH ₂ (bottom)	Ring	CH ₂ (top)	S (top)	H	
BM	0.03	-	0.18	-0.0	-	-	-	
PMBM	0.07	0.29	0.39	0.18	-	-	-	
XYL	(a)	0.10	-0.26	0.27	-0.12	0.24	-0.40	0.18
	(b)	0.10	-	0.28	-	0.18	-0.41	0.1
	(c)	0.11	-	0.28	-	0.18	-0.40	0.1
	(d)	0.10	-	0.28	-	0.25	-0.41	0.1
TM	(a)	0.09	- 0.30	0.44	- 0.31	0.31	-0.42	0.1 9
	(b)	0.09	- 0.31	0.44	- 0.25	0.22	-0.36	0.1 7
	(c)	0.09	- 0.30	0.41	- 0.23	0.22	-0.35	0.1 7
	(d)	0.09	- 0.30	0.44	- 0.27	0.26	-0.40	0.1 9

In each case, the total charge of the Au_4 cluster is small, indicating that Au-S charge separation contributes very little to the overall dipole moment. The largest dipole contributions in the monothiols come from the S^- -CH₂⁺ charge separation and μ_z is determined by the orientation of the molecule relative to the surface normal.

Note, from Eq. (1), that only the

component of the dipole vector is relevant for the

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Table 1. Dipole moments (in Debye) of the molecules studied.

Molecule μ

X

$|\mu|$ BM –1.35 0.20 2.20 2.59 PMBM 0.34 –0.34 3.24 3.28 XYL (a) 1.88 –0.09 1.71 2.54 (b) 1.79 –1.52 3.09 3.88 (c) –0.99 –0.84 1.17 1.75 (d) 0.47 –1.59 0.27 1.68 TMXYL (a) 2.00 0.63 1.34 2.49 (b) 2.13 0.12 3.02 3.69 (c) –0.96 –0.14 1.58 1.85 (d) 0.29 0.59 0.52 0.84

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Table 2. CHelpG charge distributions for the molecules studied.

Molecule Au

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μ

Y

μ

Z

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2 (botto

(botto m)

m)

CH

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S (top)

(top)

H

BM 0.03 – 0.18 –0.0 – – –

PMBM 0.07

Ring

-

XYL (a) 0.10 –0.26 0.27 –0.12 0.24 –0.40 0.18

(b)

–

– 0.29 0.39

0.18 – –

0.10 – 0.28 – 0.18 –0.41 0.1

(c)

0.11 – 0.28 – 0.18 –0.40 0.1

(d)

0.10 – 0.28 – 0.25 –0.41 0.1

TM (a)

0.31 –0.42 0.1

9 (b)

0.09 –

0.44 – 0.30

0.31

0.22 –0.36 0.1

7 (c)

0.09 –

0.44 – 0.31

0.25

0.22 –0.35 0.1

7 (d)

0.09 –

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9

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4

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The largest dipole contributions in the monothiols come from the S—CH

2

+ charge separation and

Z

is determined by the orientation of the molecule relative to the surface normal.

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2

Z

Table 3. Relative energies (in kcal/mol) of the four conformers of the dithiols adsorbed on Au₄.

	(a)	(b)	(c)	(d)
XYL	0.00	0.75	0.30	-0.20
TMXYL	0.00	0.28	-0.98	-0.88

In summary, we have found that (a) the S^-C^+ charge separation is responsible for the large ESPs of the monothiol SAMs and (b) the mutual cancellation of the S^-C^+ dipoles as well as a specific orientation of the S^-H^+ dipole is responsible for the negligible ESPs of the dithiol SAMs[10]. From these findings, we conclude that molecular conformations are a key element in determining the electronic properties of dithiol SAMs.

Figure

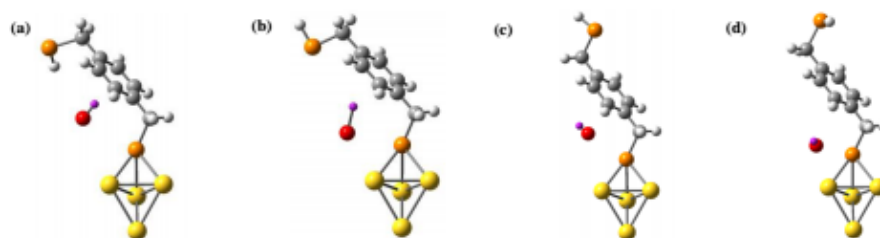


Figure 1. The optimized geometries of the four conformers of xylyldithiol (a)-(d) adsorbed on Au₄. The yellow atoms are Au, the orange atoms are S, gray are C, and white are H. The red and purple spheres indicate the negative and positive ends of the dipole vector, respectively, and the line connecting them indicates the direction and magnitude of the dipole

CONCLUSION

Since it is commonly assumed that the H atom of the S-H group[10] of thiols is lost when they form SAMs (as opposed to single molecules adsorbed on gold), the general interpretation of these observations has been that the Au^+-S^- dipole is comparable in magnitude to the terminal H^+-S^- dipole and gets cancelled in dithiols due to molecular symmetry. However, preliminary DFT calculations[11] failed to lend support to these assumptions and, in fact, yielded comparable dipole moments for both mono and dithiols. Here we report further DFT studies undertaken to examine these systems in more detail in order to develop a deeper understanding of the charge distributions in the adsorbed molecules

(a) (b) (c) (d) XYL 0.00 0.75 0.30 -0.20 TMXYL 0.00 0.28 -0.98 -0.88

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1. the the vector. The dipole orange optimized The vector, atoms vertical are geometries respectively, S, axis gray is the are of and Z-axis.

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ACKNOWLEDGMENT

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