Molecular Control of Self-Assembled Monolayer Films of Imidazole-2-thiones: Adsorption and Reactivity

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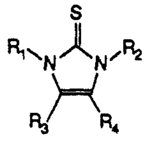
The self-assembly of hydrocarbon thiol, sulfide, and disulfide monolayers on metallic films continues to be explored as a route to the fabrication of surfaces with rationally designed interfacial structure and properties.[1] We have discovered that the thione **1** forms monolayers by self-assembly. Because up to four different substituents can be placed on the imidazole ring, **1** provides for monolayers with diverse functionality in molecularly controlled proportions.[2] We report here preliminary results on the formation of monolayers of imidazole-2-thiones **1a–g** and a novel intercalation property that results from the presence of voids between the alkyl chains in the monolayers.



1a; $R_1 = R_2 = -(CH_2)_2C_8F_{17}$; $R_3 = R_4 = H$
1b; $R_1 = Me$; $R_2 = -(CH_2)_2C_8F_{17}$; $R_3 = R_4 = H$
1c; $R_1 = -(CH_2)_2C_8H_{17}$; $R_2 = -(CH_2)_2C_8F_{17}$; $R_3 = R_4 = H$
1d; $R_1 = R_2 = -(CH_2)_2C_8H_{17}$; $R_3 = R_4 = H$
1e; $R_1 = CH_3$, $R_2 = -(CH_2)_{11}OH$; $R_3 = R_4 = H$
1f; $R_1 = -(CH_2)_2C_8H_{17}$, $R_2 = -(CH_2)_{11}OH$; $R_3 = R_4 = H$
1g; $R_1 = -(CH_2)_2C_{12}H_{29}$, $R_2 = -(CH_2)_{11}OH$; $R_3 = R_4 = H$

$\left[F_3C-\left[CF_2\right]_7CH_2-CH_2-S-\right]_2$ **2**

$F_3C-\left[CF_2\right]_5CH_2-CH_2-SH$ **3**

Exposure (10 min) of freshly evaporated gold films to methanol solutions of the imidazole-2-thiones **1a–g**, as well as **2** and **3**, gave monolayers (by ellipsometry) that exhibited sessile contact angles consistent with the expected wetting and polarizability properties of the tail groups (Table I). The monolayers are stable indefinitely at room temperature in neat methanol or methylene chloride. The contact angles decrease in order of decreasing fluorocarbon/hydrocarbon ratio **1a** > **1b** > **1c** > **1d**. The conditions for monolayer formation differed for hydro- and fluorocarbon thiones; notably, higher concentrations of the former were required to obtain reasonable monolayer thicknesses. Better reproducibility was observed for formation of fluorocarbon thione monolayers compared to hydrocarbon thiones.

Several features are consistent with the anticipated molecular structure of the thione monolayers. The contact angle for **1g** was larger than that of **1f**, suggesting that the distance of the polar hydroxyl group from the monolayer–liquid interface has a significant effect on the wetting properties.[1g] The contact angle of a **1d** monolayer is significantly lower than that of its fluorocarbon analogue **1a** and is lower than those reported for more closely packed thiols and disulfides with hydrocarbon chains.[1] Finally, the thickness of a **1b** monolayer is less than that of **1a**, suggesting a greater degree of tilting of the **1b** fluorocarbon chains.

The molecular structure of low valent metal–thione complexes[3] suggests that the imidazole ring is probably oriented nearly parallel to the gold surface. In this orientation the imidazole ring dictates the molecular packing on the surface. Pressure–area isotherms obtained for monolayers of **1a** at the air–water interface in a

Table I. Results of Adsorption of Sulfur-Containing Species onto Gold Surfaces

compd	contact angle,[a] deg H_2O	contact angle,[a] deg hexadecane	monolayer thickness,[b] Å
1a	122	63	13.9[c]
1b	108	34	10.2[c]
1c	105	36	14.7[d]
1d	87	0	10.2[e]
1e	55	0	18.6[d]
1f	43	0	20.6[c]
1g	60	0	13.3[d]
2	118	63	20.3[f]
3	116	50	10.2[f]

[a] Sessile contact angle. [b] Monolayer thicknesses were estimated by ellipsometry using refractive indices as follows: **1a** (1.26), **1b** (1.30), **1c** (1.36), **1d** (1.46), **1e** (1.46), **1f** (1.46), **1g** (1.46), **2** (1.26), **3** (1.26). [c] Values obtained upon adsorption from 1 mM CH_3OH solutions. [d] Values obtained upon adsorption from 10 mM CH_3OH solutions. [e] Values obtained upon adsorption from 1 mM *n*-hexane solutions. [f] Values obtained upon adsorption from 1 mM CH_2Cl_2 solutions.

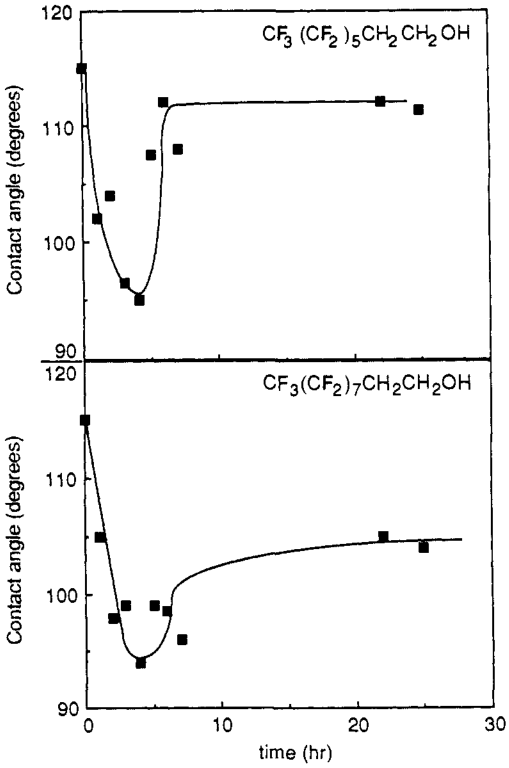


Figure 1. Sessile contact angle dependence on time of immersion of gold–**1a** monolayers in $C_6F_{13}CH_2CH_2OH$ (upper) and $C_8F_{17}CH_2CH_2OH$ (lower).

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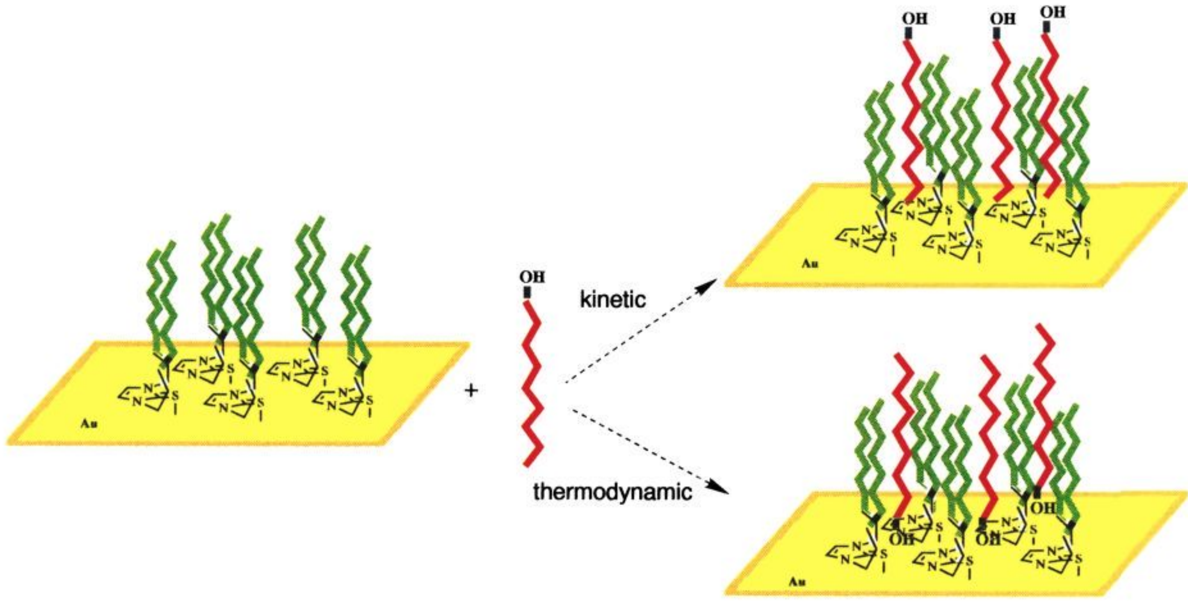
(1) (a) Blackman, L. C. F.; Dewar, M. J. S. *J. Chem. Soc.* **1957**, 162–169. (b) Blackman, L. C. F.; Dewar, M. J. S. *J. Chem. Soc.* **1957**, 171. (c) Blackman, L. C. F.; Dewar, M. J. S.; Hampson, H. *J. Appl. Chem.* **1957**, *7*, 160. (d) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559. (e) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4483. (f) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365. (g) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897. (h) Bain, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 3665. (i) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358. (j) Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426.

(2) The nonscrambling molecularity provided by **1** offers monolayer design advantages over previous routes to mixed monolayers; see: (a) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155. (b) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164. (c) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.

(3) (a) Hussain, M. S.; Isab, A. A. *Transition Met. Chem.* (*Weinheim*) **1984**, *9*, 398. (b) Hussain, M. S.; Isab, A. A. *Transition Met. Chem.* (*Weinheim*) **1984**, *10*, 178. (c) Hussain, M. S.; Isab, A. A. *J. Coord. Chem.* **1985**, *14*, 17. (d) Mak, T. C. W.; Jasim, K. S.; Cheih, C. *Inorg. Chim. Acta* **1985**, *155*, 31.

0002-7863/90/1512-6153$02.50/0

Scheme I



Langmuir trough indicated a molecular area of 62 Å², consistent with the value of 66 Å² predicted from the area of the imidazole ring. Recent reports indicate that fluorocarbon chains in Langmuir–Blodgett monolayers and stretched films of PTFE form hexagonal lattices with molecular area projections of approximately 28 Å² for the fluorocarbon chains.[4] Using this value, when $R_3 = R_4 = H$, molecular models based on nearly hexagonal packing indicate that a **1a** monolayer should have loosely packed fluorocarbon chains, in contrast to previously reported closely packed monolayers. The models also indicate 23-Å² voids between fluorocarbon chains when the chains are oriented normal to the surface. Monolayer of **1b** also are predicted to possess voids, although the area of the voids depends on the type of packing arrangement.

The indication of voids suggested that monolayers prepared from **1a** may be capable of incorporating other fluorocarbon chains via intercalation. In support of this hypothesis we have found that exposure of gold–**1a** monolayers to either $C_6F_{13}CH_2CH_2OH$ or $C_8F_{17}CH_2CH_2OH$ (1 mM in CH_3OH) results in a gradual decrease in contact angle, approaching 85–90°, without any appreciable changes in the monolayer thickness. Surprisingly, the trend of decreasing contact angle reversed after several hours and *increased* to values near that of the original monolayer (Figure 1). We attribute this behavior to initial kinetically favored intercalation of the prefluoroalkyl end of the alcohols, which results in low contact angles at early times due to a surface partially substituted with hydroxyl groups. At longer times, thermodynamically preferred intercalation of the alcohol end ultimately results in a perfluoroalkane interface (Scheme I). The latter orientation may be assisted by polar interactions of the alcohol functionality with the thione head group at the base of the monolayer. In contrast, treatment of **1b** monolayers with $C_6F_{13}CH_2CH_2OH$ and $C_8F_{17}CH_2CH_2OH$ gave only monotonically decreasing contact angles with final values of 67° and 53°, respectively, even after several days. The different behavior observed for **1a** and **1b** suggests that involvement of subtle interchain interactions may be important. Notably, treatment of the closely packed monolayers prepared from **2** and **3** with these alcohols did not cause changes in their contact angles.

Gold-**1a** and gold–**1b** monolayers are readily displaced by thiones with polar functionality at the terminus of the tail groups such as in **1e**, **1f**, and **1g**.[5] Additionally, preliminary exchange experiments show that the relative binding strength of the reagents described here decreases in the order thiols > disulfides > thiones. Preliminary experiments with a quartz crystal microbalance (QCM)[6] plated with gold electrodes revealed monotonic frequency decreases over several hours upon exposure to **1a**–**c**, **2**, and **3**, consistent with an increase in mass on the gold film, although the frequency changes were much larger than expected for monolayer formation. Further details will be reported at a later date.

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Supplementary Material Available: Details of exchange experiments and preliminary QCM data with figures (6 pages). Ordering information is given on any current masthead page.

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[4] (a) Wolf, S. G.; Deutsch, M.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Kjaer, K.; Als-Nielsen, J. *Science* **1988**, *242*, 1286. (b) Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549. (c) Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119.

[5] The preliminary exchange experiments were performed simply by immersion of a monolayer (on gold) in a 1 mM solution of a different sulfur-containing reagent for several hours. For example, thiones with polar tail groups (**1e**, **1f**, **1g**) readily displace monolayers of thiones with nonpolar tail groups (**1a**, **1b**). Thiones with polar tail groups, however, will not displace monolayers of the disulfide **2** or thiol **3**. Conversely, monolayers of the thiones with polar tail groups are readily displaced by **2** and **3**. Presently, we cannot infer whether these observations reflect kinetic or thermodynamic factors.

[6] (a) Saeurbrey, G. *Z. Phys.* **1955**, *155*, 206. (b) Ward, M. D.; Buttry, D. A. *Science*, in press.