

# Langmuir

Langmuir, 1997, 13(14), 3769-3774, DOI:[10.1021/la960561x](https://doi.org/10.1021/la960561x)

## Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

## Supplementary material

**General Methods.**  $^1\text{H}$ -NMR spectra were recorded with a Bruker AC 250 (250 MHz). Chemical shifts are reported in parts per million (ppm) downfield to TMS. Fast atom bombardment (FAB) mass spectra were recorded with a Finnegan MAT 90. m-NBA was used as a matrix.

### **Synthesis.**

All reagents were of the highest commercially available quality and used without further purification, except for the fluorinated alcohols which were purified by distillation.

**(3) Bis-(2, 2'-(Perfluorooctanoyloxy)ethyl) Disulfide** can be obtained in the reaction of 2.00 g bis (2-hydroxyethyl) disulfide (Merck), 3.74 g perfluorooctanoyl chloride (Riedel de Haen), 1.40 g pyridine in 25 ml dichloromethane at  $0^\circ\text{C}$ . The mixture was poured on ice after stirring at room temperature for 5 hours, and extracted with 3 x 20 ml  $\text{CH}_2\text{Cl}_2$ . After washing with dilute aqueous HCl and water, the organic phase was dried over  $\text{Na}_2\text{SO}_4$ . The crude product was purified by flash chromatography (silica, chloroform). Both mono- and diester can be obtained.

Yield: 48%. Characterization: white solid;  $R_f$  ( $\text{CHCl}_3$ ): 0.70.  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] 4.60 (t, 4H, O- $\text{CH}_2$ ); 3.00 (t, 4H, S- $\text{CH}_2$ ).

Elemental anal. Calcd. (for  $\text{C}_{20}\text{H}_8\text{F}_{30}\text{O}_4\text{S}_2$ , 946.37 g/mol): C, 25.4; H, 0.9; S, 6.8. Found: C, 25.3; H, 0.9; S, 6.6. FAB-Mass:  $m/z$  = 945.9.

**(5) 3,3'-Dithiopropionic acid-(1H,1H,2H,2H-perfluorooctylester)** was obtained by reacting 0.50 g 3,3'-dithiopropionic acid with 1.82 g 1H,1H,2H,2H-perfluorooctanol (Fluorochem), 1.03 g DCC and 0.05 mg DMAP in 20 ml dichloromethane for 24 hours at room temperature. Purification of the reaction mixture by flash chromatography (eluent =  $\text{CHCl}_3$ ) gave 1.81 g 3,3'-dithiopropionic acid-(1H,1H,2H,2H-perfluorooctylester) .

Yield: 84%. Characterization: white solid;  $R_f$  ( $\text{CHCl}_3$ ): 0.57.  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] 4.41 (t, 4H, O- $\text{CH}_2$ ); 2.90 (t, 4H, S- $\text{CH}_2$ ); 2.75 (t, 4H, CO- $\text{CH}_2$ ); 2.4-2.6 (m, 4H,  $\text{CF}_2$ - $\text{CH}_2$ ).

Elemental anal. Calcd. (for  $\text{C}_{22}\text{H}_{16}\text{F}_{26}\text{O}_4\text{S}_2$ , 902.47 g/mol): C, 29.3; H, 1.8; S, 7.1. Found: C, 29.3; H, 1.6; S, 7.4. FAB-Mass:  $m/z$  = 901.9.

(6) **3,3'-Dithiopropionic acid-(1H,1H-perfluoroheptylester)** was obtained by reacting 0.50 g 3,3'-dithiopropionic acid with 1.57 g 1H,1H-perfluoroheptanol (Fluorochem), 1.03 g DCC and 0.03 mg DMAP in 20 ml dichloromethane for 24 hours at room temperature. Purification of the reaction mixture by flash chromatography (eluent =  $\text{CHCl}_3$ ) gave 1.82 g 3,3'-dithiopropionic acid-(1H,1H,2H,2H-perfluorooctylester).

Yield: 87%. Characterization: white solid;  $R_f$  ( $\text{CHCl}_3$ ): 0.58.  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] 4.56 (t,  $\text{CF}_2$ - $\text{CH}_2$ ); 2.88 (m, 4H, S- $\text{CH}_2$ ); 2.77 (m, 4H, CO- $\text{CH}_2$ ).

Elemental anal. Calcd. (for  $\text{C}_{20}\text{H}_{12}\text{F}_{26}\text{O}_4\text{S}_2$ , 874.41 g/mol): C, 27.5; H, 1.4; S, 7.3. Found: C, 27.3; H, 1.4; S, 7.2. FAB-Mass:  $m/z$  = 873.9.

(7) **2-(Perfluorodecanoylamino)ethyl thiol** was obtained in the reaction of 0.37 g cysteamine (Fluka) with 1.30 g ethyl perfluorodecanoate<sup>1</sup> in 10 ml dry diethylether. After addition of 5 drops triethylamine the mixture was stirred for 2 days. After evaporation of the solvent the residue was taken up with chloroform. The crude product was purified by column chromatography on silica (eluent =  $\text{CHCl}_3$ ).

Yield: 29%. Characterization: white solid;  $R_f$  ( $\text{CHCl}_3$ ): 0.30.  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] 6.75 (s, 1H, NH); 3.51 (m, 2H, N- $\text{CH}_2$ ); 2.68 (m, 2H,  $\text{CH}_2$ ); 1.31 (t, 1H, SH).

$\text{C}_{12}\text{H}_6\text{F}_{19}\text{NOS}$ , 573.23 g/mol: FAB-Mass:  $m/z$  = 571.8.

(1) The ethylesters of the corresponding perfluoroalkanoic acid (Riedel de Haen, Acros) were prepared by refluxing the acid in dry ethanol /  $\text{H}_2\text{SO}_4$  conc. for 24 hours, and subsequent extraction of the reaction mixture and added ice with diethyl ether.

**(9) 2-(Perfluorooctanoylamino)ethyl thiol** was obtained in the reaction of 1.00 g cysteamine (Fluka) with 2.50 g ethyl perfluorooctanoate<sup>1</sup> in 15 ml dry diethylether. After addition of 5 drops triethylamine the mixture was stirred for 2 days. After evaporation of the solvent the residue was taken up with chloroform. The crude product was purified by column chromatography on silica (eluent = CHCl<sub>3</sub>).

Yield: 29%. Characterization: white solid;  $R_f$  (CHCl<sub>3</sub>): 0.40. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 6.75 (s, 1H, NH); 3.51 (m, 2H, N-CH<sub>2</sub>); 2.68 (m, 2H, CH<sub>2</sub>); 1.31 (t, 1H, SH).

C<sub>10</sub>H<sub>6</sub>F<sub>15</sub>NOS, 473.21 g/mol: FAB-Mass:  $m/z$  = 473.0.

**Figure 1**

AFM image ( $1.0\ \mu\text{m} \times 1.0\ \mu\text{m}$ ) of sputtered gold on mica, measurement performed in air.

**Figure 2**

AFM image of an Au (111) patch on sputtered gold ( $2.3 \times 2.3\ \text{nm}$ ), measurement performed in air.

**Figure 3**

Histograms of measured lattice constants of SAMs of compounds **1** - **6**, and **10**.

## Supplementary Material

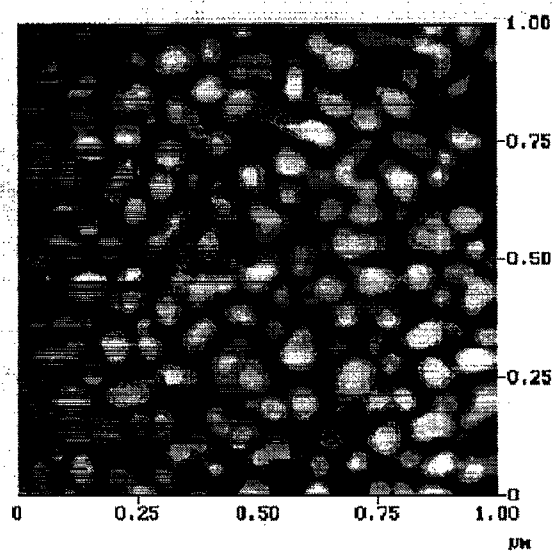


FIGURE 1

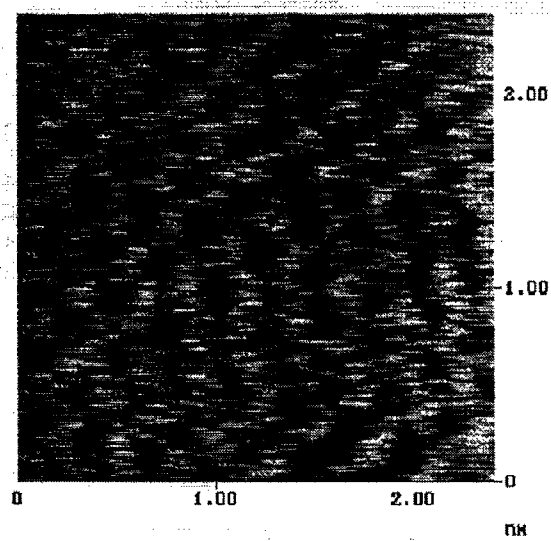


FIGURE 2

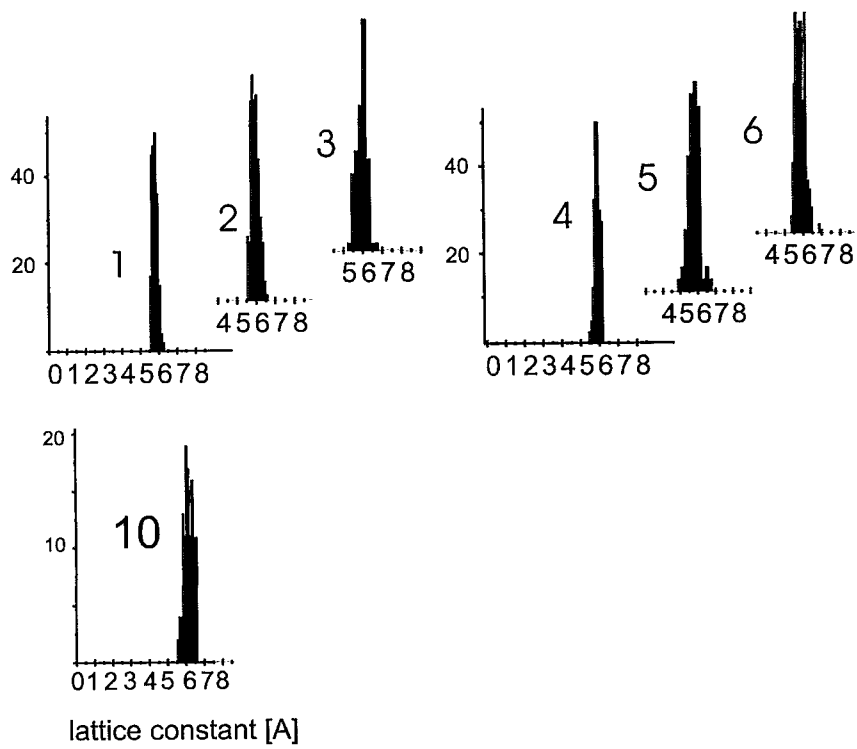


FIGURE 3