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Supplementary material

General Methods. ^{1}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°C. The mixture was poured on ice after stirring at room temperature for 5 hours, and extracted with 3 x 20 ml CH_2Cl_2. After washing with dilute aqueous HCl and water, the organic phase was dried over Na_2SO_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 ($CHCl_3$): 0.70. ^{1}H-NMR (250 MHz, $CDCl_3$): δ [ppm] 4.60 (t, 4H, O-CH_2); 3.00 (t, 4H, S-CH_2).

Elemental anal. Calcd. (for $C_{20}H_8F_{30}O_4S_2$, 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 = $CHCl_3$) gave 1.81 g 3,3'-dithiopropionic acid-(1H,1H,2H,2H-perfluorooctylester) .

Yield: 84%. Characterization: white solid; R_f ($CHCl_3$): 0.57. ^{1}H-NMR (250 MHz, $CDCl_3$): δ [ppm] 4.41 (t, 4H, O-CH_2); 2.90 (t, 4H, S-CH_2); 2.75 (t, 4H, CO-CH_2); 2.4-2.6 (m, 4H, CF_2-CH_2).

Elemental anal. Calcd. (for $C_{22}H_{16}F_{26}O_4S_2$, 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 = $CHCl_3$)gave 1.82 g 3,3'-dithiopropionic acid-(1H,1H,2H,2H-perfluorooctylester) .

Yield: 87%. Characterization: white solid; R_f ($CHCl_3$): 0.58. ^{1}H-NMR (250 MHz, $CDCl_3$): δ [ppm] 4.56 (t, CF_2-CH_2); 2.88 (m, 4H, S-CH_2); 2.77 (m, 4H, CO-CH_2).

Elemental anal. Calcd. (for $C_{20}H_{12}F_{26}O_4S_2$, 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[1] 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 = $CHCl_3$).

Yield: 29%. Characterization: white solid; R_f ($CHCl_3$): 0.30. ^{1}H-NMR (250 MHz, $CDCl_3$): δ [ppm] 6.75 (s, 1H, NH); 3.51 (m, 2H, N-CH_2); 2.68 (m, 2H, CH_2); 1.31 (t, 1H, SH).

$C_{12}H_6F_{19}NOS$, 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 / H_2SO_4 conz. 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[1] 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 = $CHCl_3$).

Yield: 29%. Characterization: white solid; R_f ($CHCl_3$): 0.40. ^{1}H-NMR (250 MHz, $CDCl_3$): δ [ppm] 6.75 (s, 1H, NH); 3.51 (m, 2H, N-CH_2); 2.68 (m, 2H, CH_2); 1.31 (t, 1H, SH).

$C_{10}H_6F_{15}NOS$, 473.21 g/mol: FAB-Mass: m/z = 473.0.

Figure 1

AFM image (1.0 μm × 1.0 μm) of sputtered gold on mica, measurement performed in air.

Figure 2

AFM image of an Au (111) patch on sputtered gold (2.3 × 2.3 nm), measurement performed in air.

Figure 3

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

Supplementary Material

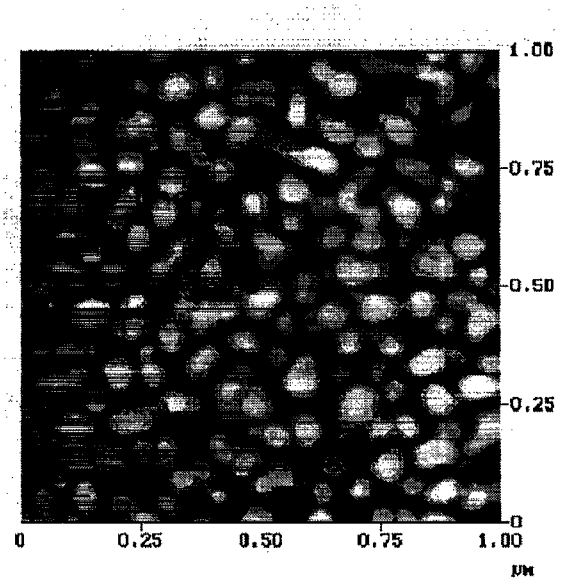


FIGURE 1

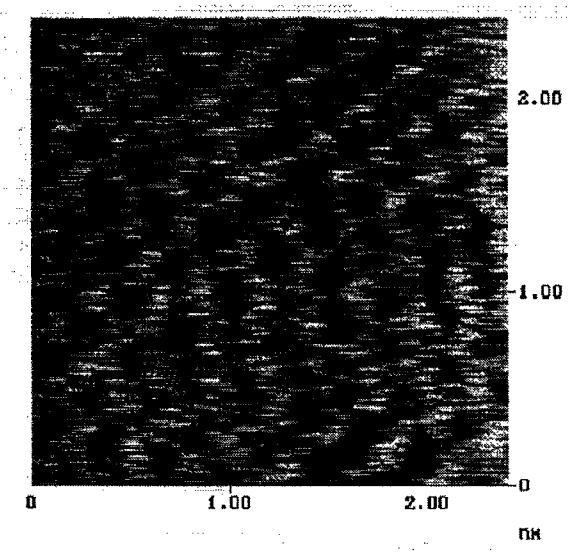
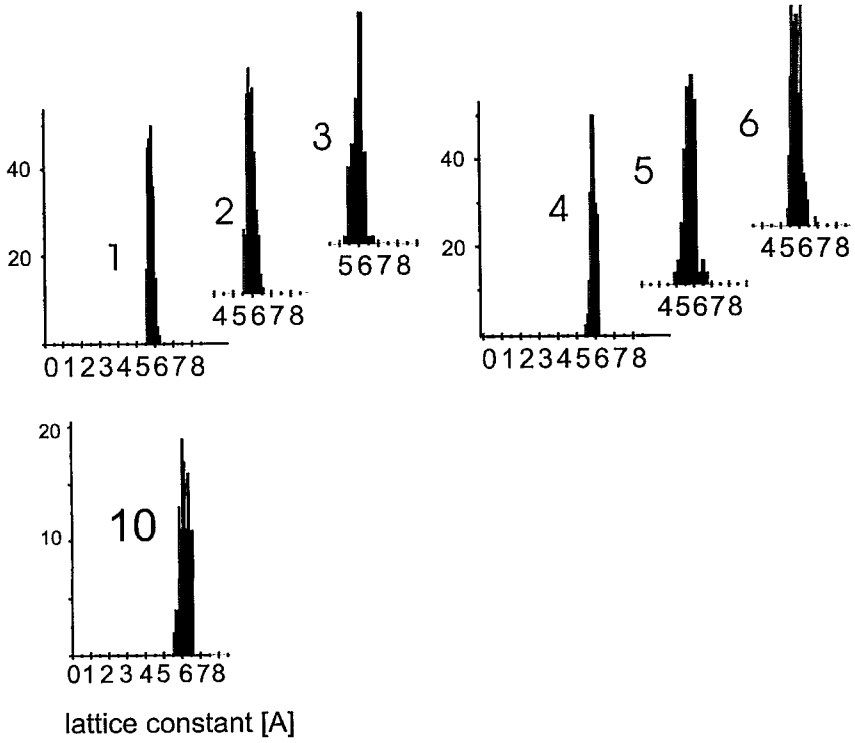


FIGURE 2


40
20
1
2
3
45678
5678
012345678
4
5
6
45678
45678
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20
10
10
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lattice constant [A]

FIGURE 3