Ionic strength mediated hydrophobic force switching of CF_3-terminated ethylene glycol self-assembled monolayers (SAMs) on gold†

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We have synthesised novel oligo(ethylene glycol), CF_3-terminated switching self-assembled monolayers, which allow the force experienced by a hydrophobic object to be controlled *via* the ionic strength of the environment.

Alkane-thiol based self-assembled monolayers (SAMs) have seen an ever increasing level of interest since they were first introduced more than two decades ago. Part of their attraction is due to the ease of their preparation in combination with the great flexibility they offer to create concentrated planes of functionality by modifying the surfactant molecules. One prominent example are oligo(ethylene glycol) (OEG)-terminated alkanethiol SAMs. They have been shown to resist the non-specific adsorption of some proteins[1,2] and hence are of significant interest in the life sciences and related areas. Inspired by their protein repelling properties several studies were carried out to determine the underlying mechanisms and the interactions involved, *e.g.* refs. 3–9. It had been observed that the protein adsorption increases with the hydrophobicity of the substrate.[1,2] Mixed films of hydrophobically and OEG terminated surfactants were prepared to study the influence of these functionalities on protein adsorption properties.[10] Other studies reported on the force between charged and hydrophobic probes and the monolayer films.[6,7] The forces measured with a hydrophobic probe (attraction or repulsion) were found to correlate with the protein adsorption properties of the films (adsorption or resistance to adsorption).[5,7] The forces indicated the existence of an electrical double layer,[5–7,11] suggesting that an electrostatic component is involved. This has been confirmed by theoretical calculations.[12,13]

Here we report on several surfactant films based on oligo(ethylene glycol) modified alkanethiols that switch between an attractive and a repulsive force on approach with a hydrophobic probe depending on the ionic conditions of the environment. Recently, a significant level of interest has emerged in SAMs with dynamic properties, in particular those with switching properties. External switching parameters such as an electric field,[14,15] pH,[16] or temperature have been explored in connection with SAMs.[17] The ionic strength is an external parameter that can be easily controlled. The films presented here are interesting for the reversible immobilisation of hydrophobic (nano)particles and in colloidal chemistry. Similar surfactants might become important in bio-related fields and in connection with biosensors since they have the potential to adsorb/immobilise proteins reversibly if the switch can be tailored to occur at an ionic strength that is compatible with proteins.

The surfactants we have synthesized are OEG-modified alkanethiols with three or four ethylene glycol units, and with a hydrophobic trifluoropropyl or trifluorobutyl group on top, here referred to as molecules **1**, **2** and **3**, and shown in Fig. 1. These surfactants allow the systematic study of the influence of increasing hydrophobicity (**1** *vs.* **2**) or additional OEG groups (**1** *vs.* **3**) on the force experienced by an object approaching the surfaces.

The surfactants were synthesised following the synthetic route illustrated in Fig. 2 and similar to the one reported in ref. 18 (see ESI† for details on the synthesis).

The required SAMs were prepared by immersing gold substrates (50 nm thick evaporated gold films on Si wafers primed with 5 nm Cr as an adhesion promoter) into 1 mM solutions of **1–3** in dimethylformamide for 12–16 h. The films were subsequently characterized by photoelectron spectroscopy (XPS), ellipsometry, contact angle measurements, and atomic force spectroscopy. All measurements were performed at room temperature.

The XPS survey spectra showed the presence of carbon, oxygen, fluorine and gold as expected. Elemental ratios were determined from single region spectra. All ratios (C/O, C/F, O/F, $C_{ether}/C_{aliphatic}$) were close to the expected values with no indication for the presence of a significant amount of contamination. The results compare well to those published for similar molecules in the literature.[9] Detailed results are given in the ESI.† The resulting densities of molecules on the surface were extracted from the measured C/Au signal ratios using an octadecanethiol and a dodecanethiol film as a reference.[9] The values obtained are 77, 81 and 73% for **1**, **2** and **3**, respectively. They are in agreement with results reported for similar methyl terminated films.[9]

The ellipsometry measurements of the SAMs gave thickness values of 1.8 nm for **1**, 1.9 nm for **2**, and 2.0 nm for **3**. A value of

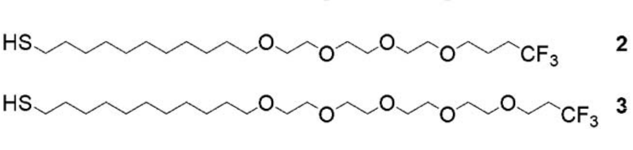

Fig. 1 Schematic of the three surfactants synthesised: (1-mercaptoundec-11-yl)tri(ethylene glycol) 3,3,3-trifluoropropyl ether (**1**), (1-mercaptoundec-11-yl)tri(ethylene glycol) 4,4,4-trifluoro-*n*-butyl ether (**2**) and (1-mercaptoundec-11-yl)tetra(ethylene glycol) 3,3,3-trifluoropropyl ether (**3**).

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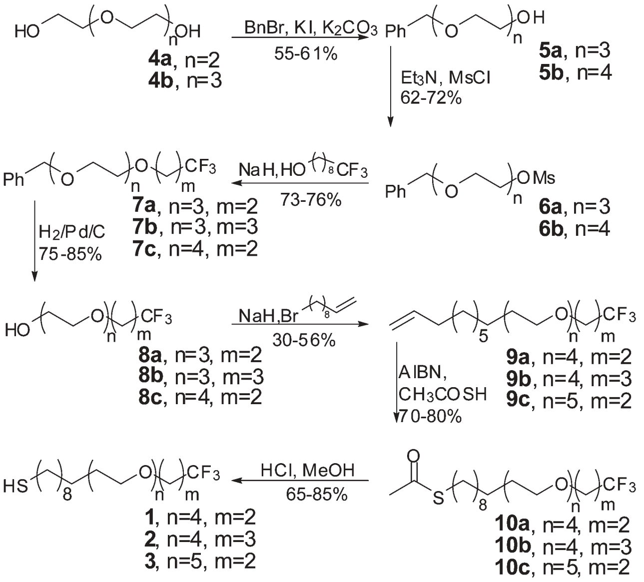

Fig. 2 General synthetic pathway for the (mercaptoundec-11-yl)-poly(ethylene glycol) trifluoro alkyl ether surfactants.

1.45 was used for the refractive index of the organic films.[10] Compared to the theoretical lengths of the molecules of 2.64, 2.76 and 2.92 nm, and taking into account that the alkane chains are tilted similar to alkanethiol films,[19] the resulting packing density for the films relative to a dodecanethiol SAM can be determined to be around 81, 82 and 82%, respectively. These values are consistent with those obtained from XPS.

The average advancing water contact angle values obtained were 93, 96 and 94° for **1**, **2** and **3**, respectively. Values for the CH_3-terminated counterparts of **1** and **2** are 94 and 107°, respectively.[9] Our results indicate similarly densely packed films with a significant fraction of hydrophobic groups exposed. The addition of one CH_2 group (**1** *vs.* **2**), however, appears to have a smaller effect on the hydrophobicity in the case of our CF_3-terminated surfactant, where only a moderate increase from 93 to 96° was found.

Force measurements on these films were performed with AFM tips coated by thermally evaporating a nickel/chromium mixture (5 nm) as an adhesion promoter followed by 50 nm of gold. Probes were made hydrophobic by deposition of a dodecanethiol self-assembled monolayer from solution. The hydrophobicity of the tips was checked by recording force–distance curves on an dodecanethiol SAM under electrolyte solution at different concentrations. The results indicated hydrophobic and stable probes (see ESI†). Force–distance curves on the films prepared from the synthesised molecules were measured in KNO_3 solutions of different concentrations. Fig. 3 shows the forces experienced by a probe upon approaching the different surfaces and depending on the distance between the probe and surface. These curves are obtained by converting the measured cantilever deflection *vs.* piezo displacement curves as previously described.[20] Zero distance corresponds to a hard-wall potential. Fig. 3 displays typical results obtained after averaging 10 curves.

At low KNO_3 concentrations the force experienced by the hydrophobic tip was repulsive for all prepared SAMs. When the ionic strength was increased a switch from repulsion to attraction was observed. This switch occurred, however, at different concentrations for the different films. It was between 1 and 10 mM for **1**, below 1 mM for **2**, and between 10 and 100 mM for **3**. The decay lengths of the forces were determined from exponential fits to the data and found to be in accordance with the expected Debye lengths based on the ionic strengths of the solution for concentrations of 1 mM and above.[21] Note that for lower than 1 mM concentrations a deviation from the theoretical Debye length has been observed before[6] and is likely due to dissolved CO_2. The actual ion concentration will therefore be higher.

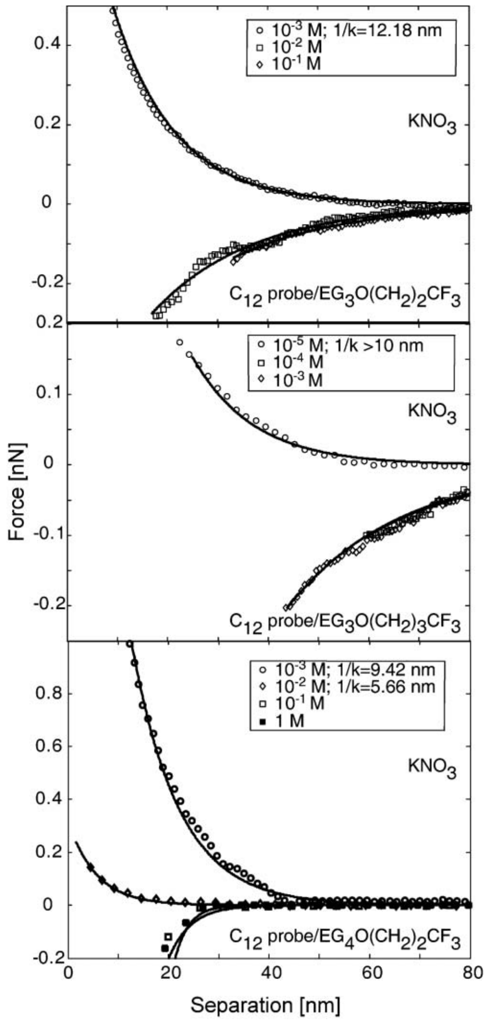

Fig. 3 Force–distance curves recorded in KNO_3 solutions of different concentrations with a hydrophobic probe on approach of the SAMs of the three surfactants synthesised. Top: surfactant **1**; middle: **2**, bottom: **3**. $1/\kappa$ indicates the experimental Debye lengths of the repulsive forces.

The force experienced by the hydrophobic tip is a superposition of the hydrophobic attraction, which is independent of the ionic strength, and a repulsive electrostatic component due to the OEGs and the electrolyte that depends on the ionic strength.[7] The latter is screened in high ionic concentrations, *i.e.*, it is of short range. As a result, the long range hydrophobic force dominates in highly concentrated solutions. The relative strengths are influenced by the relative amounts of hydrophobic and OEG groups in the film. The switching is therefore a consequence of the resulting electrostatic interaction between the hydrophobic probe and the OEG units in the electrolyte[7] in combination with the interaction with the hydrophobic end group.

It is likely that the trifluoromethyl group at the top causes slightly more disorder in the films than a methyl group[22] and also induces a stronger dipole moment. This is supported by the contact angle values measured for **1** and **2**. The CF_3-terminated SAMs show generally slightly lower water contact angle values than their methyl terminated counterparts which could be due to a disordering at the interface.[22] The fact that the contact angles we measure for our CF_3-terminated surfactant films are lower than those of the corresponding CH_3-terminated films therefore suggest a higher degree of disorder at the top of the molecules. This disorder will expose more of the ethylene glycol units such that the resulting films resemble more closely a 'mixed film' than their methyl terminated counterparts. Other groups have reported that discrete mixtures of hydrophobic and resistant groups coadsorbed show different amounts of protein adsorption[10] and can reversibly adsorb proteins depending on the temperature.[17] The species presented here combine both hydrophobic and hydrophilic structural elements and could obviate the need for adsorption from multicomponent solutions making the preparation of such films easier.

In summary, the present study demonstrates that the interaction between a hydrophobic probe and the prepared SAMs can be reversibly switched by changing the ionic strength of the environment. For the films presented the switch occurred at concentrations between 1 and 100 mM depending on the composition of the surfactant. The addition of a hydrophobic methylene group to the surfactant molecule shifted the switch to lower ionic strengths, while adding an ethylene glycol group moved the switch to higher concentrations. This indicates that the switching property can be tailored depending on the composition of the surfactant and suggests that a suitable ratio of hydrophobic and OEG groups might produce a switch at concentrations compatible with the natural environment of proteins.

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