Electronic Supplementary Material (ESI) for Analyst.

Switching Specific Biomolecular Interactions on Surfaces under Complex Biological Conditions

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Supporting Information

SAM characterisation

Table S1. Advancing and receding water contact angles and ellipsometric thickness for the different SAMs formed for 24 h. The theoretical molecular lengths were derived from ChemBio3D Ultra 12.0 in which the molecules were in fully extended conformations.

SAM	**Contact Angle (º)**		**Thickness (nm)**	
	Adv.	*Rec.*	*Theor.*	*Exp.*
Biotin-4KC	43 ± 2	35 ± 3	4.7	1.7 ± 0.4
C3TEG	34 ± 2	27 ± 1	1.6	1.3 ± 0.3
C11TEG	29 ± 2	25 ± 3	2.6	1.7 ± 0.2
Biotin-4KC:C3TEG	35 ± 3	32 ± 2	-	1.6 ± 0.1
Biotin-4KC:C11TEG	39 ± 2	32 ± 3	-	1.5 ± 0.1

Characterisation of the biotin-4KC:C3TEG SAMs

The **biotin-4KC:C3TEG** mixed SAM was prepared on a gold surface from a solution ratio of 1:40 of **biotin-4KC:C3TEG**. The mixed SAMs have been previously[1] characterized by XPS, which was shown to afford a **biotin-4KC:C3TEG** surface ratio of 1:16 ± 4. In turn, this surface ratio was demonstrated to be effective in providing local free volume for the conformational switching of the oligopeptides to occur on the gold surfaces, thus providing control over the biomolecular interactions on the surface. Herein, the formation of mixed **biotin-4KC:C3TEG** SAMs was analysed by means of contact angle and ellipsometry (Table S1). As expected, the water advancing (Adv) and receding (Rec) contact angles for the **biotin-4KC:C3TEG** SAM revealed a hydrophilic monolayer, exhibiting contact angles in between those observed for pure monolayers of either components. The ellipsometric thickness of the **biotin-4KC:C3TEG** SAMs was determined to be 1.6 nm, which is also within the range observed for pure **C3TEG** and **biotin-4KC** monolayers. Note that the ellipsometric thickness of the pure

formed SAMs, is less than the theoretical molecular length of the molecules (Table S1). This discrepancy, between molecular length and SAM thickness, is expected, in agreement with the literature, and it is ascribed to both the tilt angle and density of the SAM surfactants.[2]

Characterisation of the C11TEG SAMs

C11TEG SAMs were also analysed by contact angle and ellipsometry. The contact angle of the **C11TEG** SAM is slightly lower than that of **C3TEG** SAM, with also a smaller hysteresis (θ_{Adv} -θ_{Rec}) of 4º as compared with the 7º obtained for the **C3TEG** SAM. From these results, we infer that the longer hydrocarbon chain for the **C11TEG** has led to an enhancement in the hydrophilic properties of the surface and lower hysteresis, both indicating the presence of a more close-packed monolayer. Ellipsometry analysis also confirmed the formation of **C11TEG** SAMs with thickness values close to the theoretical measurements.

XPS analysis revealed the presence of the elemental species S, C and O on the **C11TEG** SAM (Figure S1), confirming thus the formation of the **C11TEG** SAM. The S 2p spectrum (Figure S1a) consists of a doublet peak at 163.4 eV (S $2p_{1/2}$) and 162.2 eV (S $2p_{3/2}$), indicating that the sulphur is chemisorbed on the gold surface.[3] Note that no nitrogen peak was observed for pure **C11TEG** SAMs (Figure S1b). The C 1s spectrum (Figure S1c) can be deconvoluted into two peaks, which are attributed to three different binding environments. The peak at 285.5 eV is attributed to C-C bonds,[4] while the peak at 287.3 eV corresponds to C 1s of the two binding environments of C-S and C-O.[4] The O 1s spectrum (Figure S1d) consists of one peak, arising from the C-O (533.8 eV) bonds.[4]

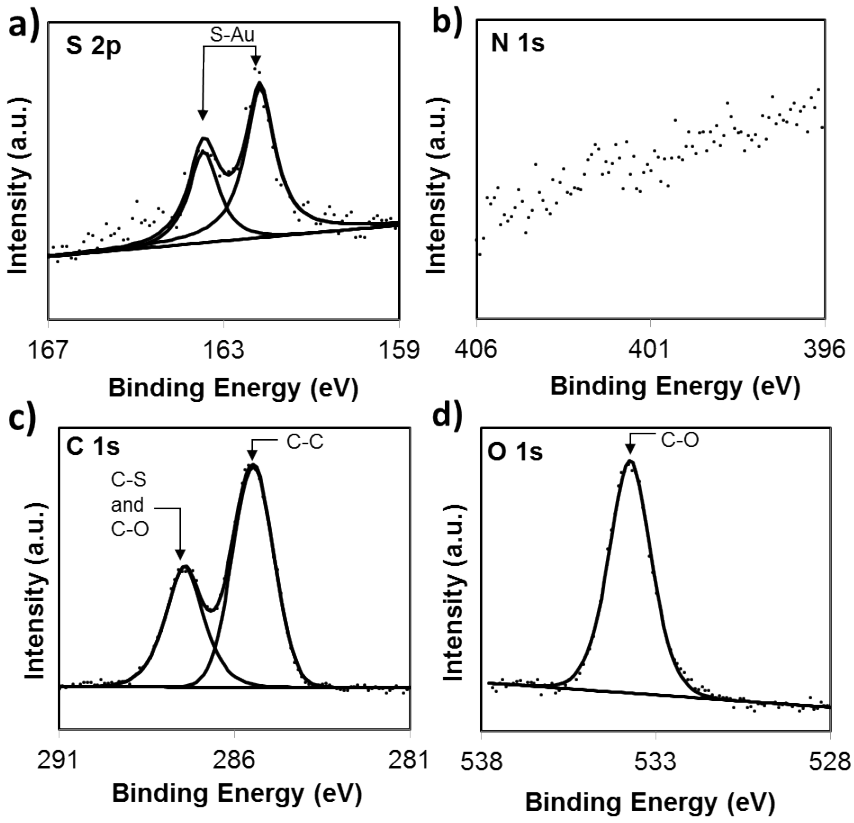

Figure S1. XPS spectra of the a) S 2p, b) N 1s, c) C 1s and d) O 1s peak regions of the **C11TEG** SAM.

Characterisation of the biotin-4KC:C11TEG SAMs

Apart from XPS data that is discussed in the main manuscript, contact angle and ellipsometry data also supported the formation of the **biotin-4KC:C11TEG** mixed SAM. As expected, the water advancing (Adv) and receding (Rec) contact angles for the **biotin-4KC:C11TEG** SAM revealed a hydrophilic monolayer, exhibiting contact angles in between those observed for pure monolayers of either components. The ellipsometric thickness of the **biotin-4KC:C3TEG** SAMs was determined to be 1.5 nm, which is also within the range observed for pure **C11TEG** and **biotin-4KC** monolayers.

References

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