PEPTIDE NUCLEIC ACIDS CAN FORM ORDERED SELF-ASSEMBLED MONOLAYERS ON SURFACES WITH DNA RECOGNITION CAPABILITY

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Self-assembly and self-organisation of molecules are the main strategies used in nature to permit life to emerge from its building blocks, and have inspired new trends in nanotechnology based on a bottom-up approach. Self-assembled monolayers (SAMs) of alkanethiols have been widely studied due to their relevant technological properties. Based on such knowledge, thiolated DNA has been immobilised on surfaces, although it usually forms disordered formless globular structures with reduced bioactivity, or requires the co-immobilization of spacer thiols leading to mixed monolayers.

Here we report on the formation and structural characterization of ordered SAMs of the DNA analogous peptide nucleic acid (PNA). PNA is an achiral and uncharged DNA mimic of high biological and chemical stability.

We show that, in spite of their remarkably long length of up to 7 nm, cysteine-modified ssPNA oligomers assemble by themselves standing-up on gold surfaces similarly to the SAMs of short alkanethiols. They stabilize on the surface by chain-chain interaction trough H-bonding between non-complementary nucleobases. We have found an equilibrium between lying and standing up molecules on the surface as a function of the molecular coverage. Furthermore, BioSAMs of ssPNAs maintain their capability for recognising complementary ssDNA, and their specificity is such that they act as biosensors able to discriminate even a point mutation in target ssDNA.
These structural and functional results have been obtained by a combination of powerful label-free techniques for surface characterisation such as synchrotron radiation based X-ray photoemission spectroscopy (XPS), X-ray absorption near-edge spectroscopy (XANES), atomic force microscopy (AFM) and reflection absorption infrared spectroscopy (RAIRS).

AFM images recorded in air of ssPNA P-G142 (sequence NH_2-Cys-O-O-AATCCCCGCAT-H) immobilized at 1 μM concentration on a gold surface. One individual group of molecules has been encircled in (B). (C) schematic representation of P-G142; (D) A cross-sectional profile recorded across the line in (A). (E) wide scan AFM image at 1 μM concentration (F) AFM image recorded of ssPNA P-M41 (NH_2-Cys-O-O-GCCATCTCT-H) immobilized at concentration of 0.1μM. The height of the ordered linear features is 1 nm. (G) AFM topographic images of terraces for intermediate concentrations of P-G142 showing that steps act as the nucleation sites for adsorption of the ssPNA layer.