Controlling the Structure and Hybridization of DNA on Surfaces

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Molecular biointerfaces formed between biomolecules and solid surfaces are particularly interesting and versatile surface systems in terms of the underlying physics, chemistry, and biology. A promising pathway to the rational design of biointerfaces is suggested by the successful development of self-assembled monolayers (SAMs). The initial focus is placed on investigating simple model systems that are experimentally well-defined and can be unambiguously characterized and controlled. Such model systems help to elucidate the general principles that govern the structure and function of biointerfaces. These general principles, in turn, provide rational design rules for biointerfaces.

In case of DNA, homo-oligonucleotides—chemically uniform single-stranded DNA molecules—are a natural choice of model systems, in part because their chemical uniformity simplifies the preparation and characterization of model biointerfaces. The structure of such DNA monolayers before, during, and after hybridization experiments can be characterized using complementary *ex situ* and *in situ* techniques: x-ray photoelectron (XPS), Fourier transform infrared (FTIR), and near-edge x-ray absorption fine structure (NEXAFS) spectroscopies and surface plasmon resonance (SPR) imaging.

Quantitative analysis of DNA interactions with gold surfaces led to the discovery of a new immobilization method that is based on the intrinsic affinity of adenine nucleotides for gold. This method can produce unique DNA brushes, for which grafting density and conformation are independently and deterministically controlled. DNA hybrids that include adenine blocks for attachment to gold are also proving to be an excellent model system both for elucidating the effects of surface interactions on DNA hybrids and for possible applications as self-assembled and functional DNA structures on surfaces.