

**Biomacromolecules at Nanostructured Surfaces:
from a single molecule towards a collective behavior view**

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In recent years, 1) the fact that nano-features at surfaces have a critical effect on the amount and structural state of adsorbed biomacromolecules has become a widely accepted paradigm. This idea is, in turn, connected to the wider idea that the state of the “confined” few layers at surfaces determine the “evolution” of complex processes on the covered surfaces as, for instance, extracellular matrix organization, cell seeding or bacteria colonization.

In fact, the nanoscale patterning of specific biochemical motifs has been shown to be able to influence cell adhesion and spreading, as well as differentiation and cytoskeletal organization, highlighting the close relationship between the surface nanostructures and the nanosized biochemical machinery that allows cells to respond to environmental stimuli.

In this largely phenomenological framework, the Physical Chemistry approach has a fundamental role in elucidating the critical role played by the organization, including the facts about amount, nature of the binding and conformational states, of the biomolecules “confined” at surfaces, which in turn provide the appropriate platform for the subsequent biochemical processes.

Accordingly, experimental results on the strategies of driving adsorption selectivity and proper exposure of the bioactive sites of peptides and proteins will be shortly reported, focusing examples of

(1) targeted chelation-based methodologies to anchoring well-defined amounts of oriented biomolecules [1,2],

(2) a curvature-related “geometrical” resonance of nanostructure and biomolecules size determining their adsorption [4].

(3) A case study of a stimuli-responsive system, consisting in short-chain thiolated peptides will be discussed, highlighting the collective character of the structure and response of the systems forming the “self-assembling” monolayer [5].

It is interesting to note that while the experiments [1]-[3] rely on a “single-molecule” view, i.e., looking at structure and behavior of the confined biomolecular layers in terms of mere assemblies of single-responding molecules, the experiment [4] highlighted an adjourned view of the adsorbed layer structure and behavior, as due to the whole ensemble of anchored and therefore interacting molecular systems.

This view of the action and properties of macromolecular-immobilized layers in terms of a “collective” behavior is, in our opinion, the key towards the understanding and control of the processes at functionalized surfaces.