ENGINEERING AND CHARACTERIZATION OF MOLECULAR SURFACES

Antonino Licciardello (Associate Professor)
alicciardello@unict.it

Alberto Torrisi* (Full Professor)

Valentina Spampinato (PhD Student)
Davide Sapuppo (PhD Student)
Gabriella Zappalà (PhD Student)

*Facoltà di Agraria

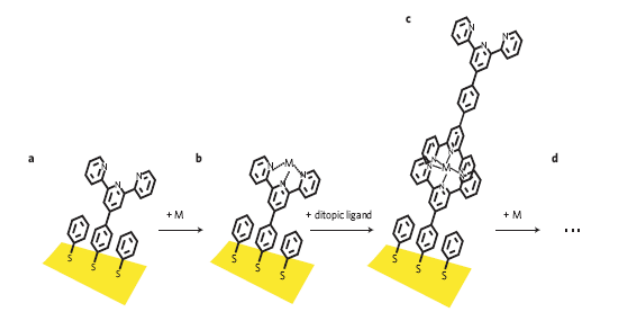

Figure 1: Stepwise assembly of molecular wires

Tailoring of surface properties is a major issue in the development of devices in the micro- and nanometre scale. Many efforts are currently produced for integrating on solid surfaces some features (*e.g.* electronic or molecular recognition properties), exhibited by isolated molecules or supramolecular systems. We are developing methodologies that transfer to the surface the approaches typical of supramolecular chemistry for the construction of functional, nanometre-sized structures. Parallel to surface modification studies, and strictly related with them, we are interested in techniques for chemical and morphological characterization of surfaces and thin films, such as photoelectron spectroscopy, secondary ion mass spectrometry, atomic force microscopy. Among others, we are currently developing methods for spatially resolved chemical characterisation of molecular materials by means time-of-flight secondary ion mass spectrometry (ToF-SIMS) and by pulsed radiofrequency glow discharge mass spectrometry (rfGDTOFMS). In this context, we are studying some fundamental aspects of interaction of plasma and polyatomic ions with organic and polymer surfaces.

Keywords: surfaces, self assembled monolayers, ToF-SIMS, cluster beams, GDMS

1. Supramolecular architectures for tailoring of surface properties

The general approach we use involves the anchoring of a self assembled monolayer of suitable molecules on the surface to be modified and to use such a layer as the base "platform" for the construction of supramolecular architectures with the desired electrical or sensor properties. For example, we have shown that a mixed component thiolate SAM on gold, containing a terpyridine ligand, is a very reproducible "platform" system that can be used as a base for subsequent surface reactions, as sketched in Figure 1 in the case of the stepwise construction of self-assembled, Fe(II)- or Co(II)-containing molecular wires, that exhibit outstanding conduction[1] and optical[2] properties. This approach has been exploited for: the direct surface synthesis of heteroleptic ruthenium complexes[3] (useful for light harvesting); the

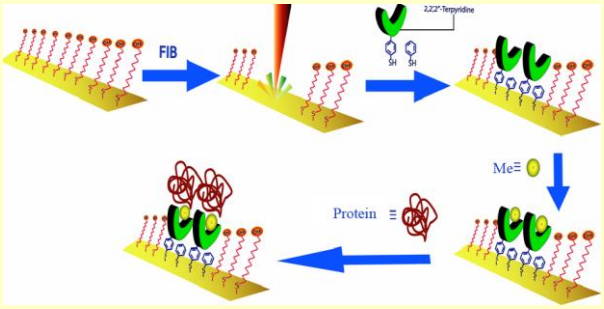

Figure 2. Scheme of the preparation of a surface capable of spatially selective adsorbtion of lactoferrin

incorporation of metal cations able to drive the specific adsorption of proteins[4] (Fig. 2); the controlled anchoring of single strand oligonucleotides capable of DNA recognition. Such approach, initially applied for modifying metal surfaces, has been recently extended to oxide based surfaces[5].

2. Molecular depth profiling of polymer materials by surface mass spectrometry techniques.

Analysis of organic and polymer-based films is fundamental in the field of materials science and it is of technological interest in many applications (paints and pigment films, coatings, poly-LED displays, organic photovoltaic systems, etc.). In many cases the knowledge of detailed molecular information along depth, i.e. 'molecular depth profiling', is required. This is presently obtained by means of secondary ion mass spectrometry using polyatomic primary ions (cluster-SIMS), but the results are strongly dependent on the particular polymer studied. We demonstrated that profiling behaviour of polymers is strongly dependent on ion-beam induced chemistry[6] and is influenced by temperature and by the presence of reactive gases, such as nitric oxide. Playing with these parameters, it is possible to disfavour adverse ion-beam induced reactions and to obtain cluster-SIMS molecular depth profiles from difficult polymers (*e.g.* polystyrene). Also, interesting results can be obtained by using, for erosion, a properly modulated plasma source. We recently showed that it is possible to achieve molecular depth profiles of various polymer layers and multilayers by means of a pulsed radiofrequency glow discharge time-of-flight mass spectrometry (rfGDTOFMS)[7], a technique we contributed to develop. This work has been awarded with the "RCM Beyond Prize" as "the innovative advance in mass spectrometric instrumentation or methodology that has had the greatest immediate impact in its particular sub-discipline over years 2009-2010".

Collaborations and Research Grants

EU project FP6, STREP-NMP n° 032202 "EMDPA"

PRIN 2008 "Ordered surface layers of photo- and redox-active molecular and supramolecular systems".

European COST Action D35, Working Group D35-0016/05 "Networks of Metal Complexes and Nanoparticles with Electronic, Magnetic and Optoelectronic Properties"

Azione Integrata Italia Spagna 2009-2010 "Metodi avanzati di spettrometria di massa per l'ottenimento di profili di profondità elementari e molecolari di materiali polimerici."

Selected Publications

1. N.Tuccitto, V.Ferri, M.Cavazzini, S.Quici, G.Zhavnerko, A.Licciardello, M.A.Rampi (2009) "Highly conductive 40-nm-long molecular wires assembled by stepwise incorporation of metal centres" Nature Materials 8, 41-46

2. Tuccitto, N.; Delfanti, I.; Torrisi, V; Scandola, F; Chiorboli, C.; Stepanenko, V.; Würtner, F; Licciardello, A. (2009) "Supramolecular self-assembled multilayers of terpyridine-functionalized perylene bisimide metal complexes" Phys. Chem. Chem. Phys. 11, 4033–4038

3. Tuccitto, N.; Torrisi, V.; Cavazzini, M.; Morotti, T.; Puntoriero, F.; Quici, S.; Campagna, S; Licciardello, A. (2007) "Stepwise Formation of Ruthenium(II) Complexes by Direct Reaction on Organized Assemblies of Thiol-Terpyridine Species on Gold" ChemPhysChem 8, 227-230.

4. Tuccitto, N.; Giamblanco, N; Licciardello, A; Marletta, G. (2007) "Patterning of lactoferrin using functional SAMs of iron complexes" Chem. Commun., 2621-2623.

5. Spampinato, V.; Tuccitto, N.; Quici, S.; Calabrese, V.; Marletta, G.; Torrisi, A.; Licciardello A. (2010) "Functionalization of Oxide Surfaces by Terpyridine Phosphonate Ligands: Surface Reactions and Anchoring Geometry" Langmuir 26, 8400–8406

6. Moellers, R; Tuccitto, N; Torrisi, V.; Niehuis, E.; Licciardello, A. (2006) "Chemical effects in C_{60} irradiation of polymers" Appl Surf Sci,252 6509–6512.

7. Tuccitto, N; Lobo, L.; Tempez, A.; Delfanti, I.; Chapon, P.; Canulescu, S.; Bordel, N.; Michler, J.; Licciardello, A. (2009) "Pulsed radiofrequency glow discharge time-of-flight mass spectrometry for molecular depth profiling of polymer-based films" Rapid Commun. Mass Spectrom. 23, 549–556.