Self Assembled nano networks of electroactive molecules:Organic synthesis,realization and tuning of electronic properties

The current limitations of the “top-down” technological processes impose new approaches, which must be controlled for the integration of physical, chemical or biochemical functions on scales lower than 100 nm. In the same way, the“bottom-up” realization based on the elaboration of functional structures containing molecular elements comes up against the difficulties of the positioning of building blocks, the control of their reactivity, their spatial organization and the realization of the associated connections. Within the framework of this double limitation to overcome, our project aims to the realization in parallel of organic structures organized at the nanometre scale, by self-assembly techniques. By elaborating nano-organized networks, we will be able to investigate the electronic properties of these objects, that is an essential analysis before their future use. The fundamental study of these objects will be made according to the knowledge necessary to their potential applications such as: i) electronics and electrochemistry on the scale of single or a few “semiconductor” molecules organized on nano-scaled networks, ii) biosensors, with in particular an application towards the sensitive detection of the hybridization of DNA strands.

More precisely, the central point of the project is firstly to realize, by an original approach, nanometre scale ordered networks of electroactive organic monolayers by the replication of a spontaneously 2D structured metallic template. The objectives are to control the molecular domain size and the space distribution of molecular islands inside the network. Secondly, electro-optical, electrochemical and biochemical properties will be studied, as a function of the molecular domains size, by local and macroscopic probes. In this multi-disciplinary project, the collaboration between two teams, specialist in the field of self-organization, either of organic molecules (ITODYS), or of metal atoms (MPQ) and the coupling to a spectroscopy team (CEA) specialist of nanometre-sized objects, will make it possible to carry out and characterize such complex molecular structures. In a very concrete way, the use of spontaneously nano-structured gold surfaces as templates will give access to the building of nano-objects networks extending on macroscopic dimensions.

The presence of specific nucleation sites on the metal surface (step edges or reconstructed sites organized in high density networks ~10 Terabits/in2), allows the deposition of metal nano-islands on these sites followed by a localized grafting related to the chemical species. We will be able to make a double assembly of molecules A and B respecting the initial nano-structure (typically, island networks with a 10nm x 2nm rectangular mesh, which can extend to the overall surface of the sample). The general structure of the proposed molecules is X-(CH2)n-Y where (n=0, 10). This structure allows the grafting and self-assembly of organic monolayers (SAM). In our case, Y is a semiconductor electroactive function for which we will measure the electronic properties according to the chemical environment, either probing the effects of the electroactive molecular domain size or probing by electrochemistry the hybridization of DNA strands located around these domains. Concretely, the first prototype network will be made of an electroactive molecule B, functionalized at one end with an oligothiophene moiety Y (aromatic group made of 3 or 4 electroactive thiophene units) and at the other end with a thiol function (X- = HS-). This electroactive molecular network will be surrounded by an aliphatic thiols environment (SAM of molecule B). The realization of this type of network requires the following stages: - preparation and control of nano-structured metal surfaces and vacuum deposition of size-controlled (1-10nm) metal islands made of cobalt atoms typically; - spontaneous oxidation of cobalt islands after a short

exposure to the ambient; - adsorption in liquid phase of molecule (A) which grafts only on bare gold, between the oxidized cobalt islands; - chemical etching of oxidized cobalt islands; - adsorption of molecule (B) fixing itself on gold in the space released by the removed oxidized metal. The as-prepared networks will be analyzed as a function of domain size: a) on the one hand, for their electronic properties. Macroscopic measurements will be achieved as well as local conductivity characterization; luminescence spectroscopy/cartography and electrochemical measurements on the Y groups will also be considered; b) on the other hand, for molecular recognition with short DNA strands. The first results obtained at the laboratory make it possible to overcome the principal technical bottlenecks or to attenuate the risks of them, thus showing the feasibility of the ordered growth of molecular nanostructures.

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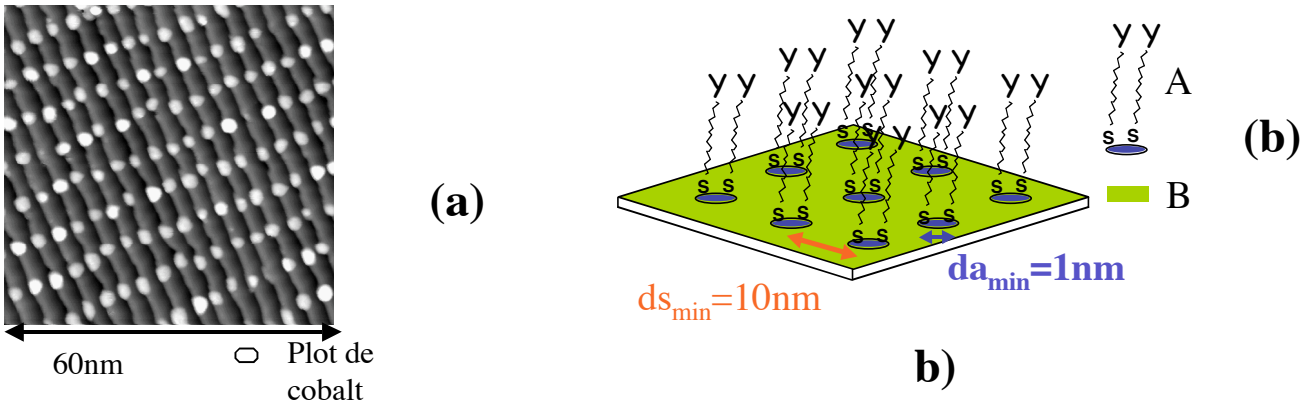

Figure 1 : scheme of the replication of the nanostructured network made of metallic islands (Co/ Au (788)) in two interpenetrated molecular networks (molecules A and B)