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## Cholesteric liquid crystal polymers with biomedical and optoelectronic application

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Cholesteric Liquid Crystal Polymers (ChLCP), synthesized in our laboratory through a stereoselective polycondensation reaction, as multifunctional optically active materials, have been extensively characterized by NMR, Raman spectroscopy, steady-state fluorescence, molecular modeling, and SAXS/WAXS. These ChLCP behave both as thermotropic and lyotropic, conferring interesting macromolecular properties indicative of potential application on the biomedical and engineering field. The amphiphilic nature of their monomers makes them polymerize along helical chains, being able to entrap smaller molecules inside, such as Lycopene. They have shown to be biocompatible against macrophages and fibroblasts cellular lines, and able to interact with biomacromolecules such as lipids (both neutral and cationic) and nucleic acids, the structures of the complexes being identified by synchrotron radiation source. Cationic liposomal/surfactant systems based on our CLCP were developed which entrapped DNA plasmids, acting as non viral cationic vectors for gene therapy, which successfully transfected in several tumor cell lines. Cationic functionalized ChLCP have been synthesized, dispersed in TAE and directly complexed with commercial DNA of increasing complexity: [Poly-A]; [Poly-C]; [Poly-G]; [PolydT]; [PolyC-PolyG]; [PolyAC-PolydT]; commercial calf thymus DNA and plasmid. Three different proportions ChLCP:DNA were prepared: (1:2), (1:1), and (2:1) respectively by mixing and digesting for 12h in a swinging shaker. The structure of the cationic complexes has been studied by SAXS at the BM16 beamline at ESRF, at room temperature. Neutron scattering experiments, had shown sufficient contrast (scattering length density difference) between new cholesteric PTOBEE-Ammonium ( $1.5$  to  $1.9 \times 10^{10}$ /cm<sup>2</sup>) and polynucleotide [PolyC-PolyG] ( $3.32 \times 10^{10}$ /cm<sup>2</sup>) for contrast variation SANS experiments. This experiment was successfully performed at NIST. These ChLCP also show optoelectronic behavior. When dispersed in solution, directly self-organize on metal and semiconductor surfaces, such as: Si(111); Pt / TiO<sub>2</sub> / SiO<sub>2</sub> / Si(001), Ag, Au, either colloidal spheres or thin layers. Under spin coating controlled conditions growth has been obtained in multilayer ordered structures. Their helical macromolecules, uncoil and get adsorbed on the metal surface, via  $\pi$ -interaction, with the aromatic rings extended parallel to the interface and the aliphatic chains directed towards the bulk solution. The interaction of these ChLCP with metals could be applied to the design of functionalized surfaces provided with physico-chemical properties of interest.

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## Nanostructured thin films: From e-tongue to fuel cell applications

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The layer-by-layer (LbL) technique is an easy, flexible and elegant bottom-up strategy that has been widely used to promote surface modification at nanoscale level, as well as for multilayer formation of advanced functional materials. We will show LbL films in sensor and fuel cell applications, exploring as well microfluidics and 3D-printing technologies. Microfluidics deals with the precise control and manipulation of liquids at the submillimetre scale, integrating research fields with emergent technologies in a cost-effective manner. 3D printing is a fully automated process offering rapid prototyping to build complex structures with high resolution without experts, with the additional potential of using materials beyond polydimethylsiloxane (PDMS) realms. The 3D printing technology can be used to facilitate the integration and fabrication of microfluidic devices, and here an e-tongue set-up was printed in less than 1h, being able to distinguish tastants below the human threshold. We also show the use of LbL films of graphene nanoplatelets in Direct Methanol Fuel Cells (DMFCs). Briefly, DMFC are promising devices for clean energy generation, however, the major impediment to commercial applications is the methanol crossover from anode to cathode. Graphene nanoplatelets of graphene oxide (GO) and reduced graphene oxide stabilized in poly(styrenesulfonic acid) sodium salt (GPSS) were LbL assembled onto Nafion<sup>®</sup> membranes in order to serve as a barrier to hamper the methanol permeation. The characterization of the modified LbL modified membranes indicated positive barrier property of the graphene nanoplatelets to the methanol permeation in a DMFC setup.

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