
**Electrochemical Activation and Control of Non-covalent Halogen Bonding in Solution and on Functionalized Electrode Surfaces.**

**Working contract:** 3 years grant - MERN T ED388 - Université Paris Diderot

**Beginning:** September - October 2016

**Place:** Laboratoire d’Electrochimie Moléculaire (LEM) UMR 7591, CNRS - Université Paris Diderot

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**Domains:** Organic chemistry, molecular electrochemistry, supramolecular chemistry.

**Key words:** halogen bonding, activation of non-covalent interactions, redox switch, modified electrodes, self-assembly.

**Context:** Halogen bonding (XB) has recently gained increasing interest in the scientific community. Halogen bonds (XB) are non-covalent interactions in which a covalently bound halogen is acting as the electrophilic species in the presence of a Lewis Base. Surprisingly the XB donor properties of organo halides (R-X; X = Cl, Br, I) have been completely neglected for a long time although many biologically active compounds (pharmaceuticals, pesticides, pollutants, hormones) are bearing halogen atoms which necessarily influence their affinity and reactivity in living organisms. The utility of XB for controlling self-assembly in the solid state was proven for various applications in crystal engineering and materials science. However, so far only few examples have been reported on XB interactions in solution and the corresponding emerging applications in anion sensing and transport, medicinal chemistry and catalysis. Our research group Synthesis and electrochemistry of molecular assemblies in the Laboratory of Molecular Electrochemistry (LEM) has been interested for several years in halogen bonding in the solid state and is now one of the pioneer groups in the field of electrochemical activation of XB. Our novel approach involves the design of electrochemically active redox probes as well as their assembly on electrode surfaces via chemisorption or covalent grafting. The group already has a strong expertise in the field of self-assembled monolayers (SAMs) and has recently developed a fast and reproducible electro-assisted method for SAM deposition on gold electrodes.

**Summary of the project:** The PhD project is based on a new concept, the electrochemical activation of halogen bonding**, which has recently been evidenced by our group. The exploration and generalization of this concept as well as its application for analytical purposes is a novel and highly innovative task. The first objective is to explore electrochemical XB activation in solution. The second objective consists in the transfer of the elaborated systems onto an electrode surface and in the study of the resulting interfacial reactivity. At this stage the project aims at introducing an electrochemical control in the molecular recognition process for the development of original and highly selective electrochemical sensors. The thesis will thus contribute to better understand the contribution of this important non-covalent interaction in molecular recognition events helping to develop innovative solutions for environmental challenges such as anion, drug and pollutant detection.

**Strategy and methodology:** This PhD project will combine 1) design and synthesis of novel electroactive XB donors and acceptors, 2) electrochemical investigation of XB formation in solution, 3) transfer of XB detection from solution onto surface. Various redox-active XB donors and acceptors (e.g. quinone, ferrocene, methylviologen derivatives) will be synthesized by the student, anticipating the possible attachment of anchoring groups for future surface coating. Electrochemical techniques will be used to study the non-covalent XB interactions in apotic and also aqueous solution. The corresponding thermodynamic affinity constants, ultimately controlling the efficiency of the molecular recognition event, will be determined. The interfacial reactivity of the obtained electro-active monolayers will be explored by cyclic voltammetry and time-resolved UV-visible-NIR spectro-electrochemistry as well as other complementary methods for surface characterization.

**Expected skills of the PhD candidate:** molecular electrochemistry, organic synthesis, surface modification.

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