

Redox switchable halogen bond donors for organocatalysis and molecular recognition

Exploring a novel non-covalent interaction via an electrochemical approach.

Working contract: 3 years grant - MERNT ED388 - Université Paris Diderot

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Place: Laboratoire d'Electrochimie Moléculaire (LEM) UMR 7591 (http://www.lem7.cnrs.fr/themes/LEM_4_en.htm)

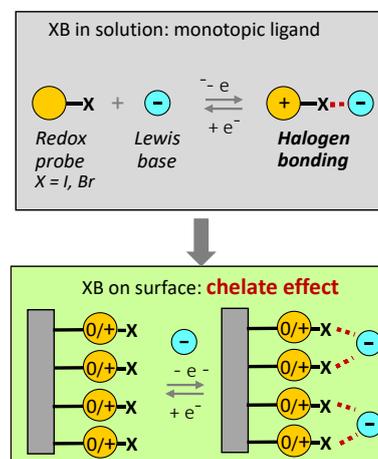
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Domains: Molecular electrochemistry, Supramolecular chemistry, Electrocatalysis, Organic chemistry

Key words: halogen bonding, activation of non-covalent interactions, Interfacial reactivity

Expected skills of the PhD candidate: molecular electrochemistry, physical chemistry, organic synthesis

Context: 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.¹ The XB donor properties of organo halides 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. Until recently, 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.² The challenge to explore XB in molecular recognition events is of high stake and some questions have never been addressed yet such as the electrochemical activation and control of XB in surface confined systems. Our research group has been working for several years on XB in the solid state³ and is now one of the leading groups in the field of electrochemical XB-activation.⁴ In fact, we have demonstrated the proof of principle for electrochemical XB switching in solution, validating that the XB-acceptor strength of a Lewis base can be controlled by the modulation of its redox state. Alternatively we have recently succeeded to tune the strength of an XB-donor in the presence of a Lewis Base. The recent development of organocatalysis based on XB has provided significant results and perspectives in organic chemistry. Huber's group, pioneer in this field,⁵ has demonstrated the involvement of XB in the catalysis of common organic reactions. Several cationic XB-donors have been developed and successfully employed as organocatalysts in Diels Alder, Michael addition and halide abstraction reactions. The catalytic activity of the respective XB donors could be correlated with the number and relative orientation of halogen substituents. Grafting this type of molecules on a well-defined surface is prawn to improve the organization and selectivity of the XB-donor ligands. Immobilization of the XB donor may offer a better control of the molecular orientation consequently increasing selectivity between XB-donor and acceptors (Figure) and also probably affects their respective catalytic activity. Moreover the catalytic reactions could be triggered by the electrochemical oxidation of an initially neutral (weak) XB-donor generating a positive charge and consequently activating the corresponding XB.



Summary of the project: This project will explore first the electrochemical activation of novel redox-switchable halogen bond donors for organo-catalysis in solution and on modified electrodes. Second, the electrochemical control of the molecular recognition properties of modified electrodes, covered with novel conducting polymers bearing XB donor moieties, will be investigated. **Both projects are promising to provide new insights into molecular recognition and the activation of covalent bonds in the view of developing original systems for applications in the fields of chemo-sensors and electro-assisted catalysis.**

Strategy and methodology: This PhD project will combine in a first part, in collaboration with Pr. S. Huber (Univ. of Bochum, Allemagne) 1) synthesize new redox-active XB redox donors 2) Analyze quantitatively XB interactions using NMR and UV-vis spectroscopy, ITC (isothermal titration calorimetry) and electrochemical techniques, 3) demonstrate electro-assisted catalytic activity and 4) graft the best identified catalyst onto the electrode surface. In a second part, in collaboration with Pr. P. Bäuerle (Univ. of Ulm, Germany), head of one of the world leading group in the fields of organic semiconducting and conducting materials, we will use conductive polymers to build up a three dimensional platform containing multiple interacting polymer-supported XB-donor sites in order to increase affinity and selectivity towards various Lewis bases. For this part, we propose to: 1) synthesize and study various bromo- or iodo-thiophene (or pyrrole), 2) use the potentiality of these compounds to form conducting polymers films on the electrode upon electrochemical oxidation and 3) explore the interfacial reactivity of the obtained electro-active modified surface.

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