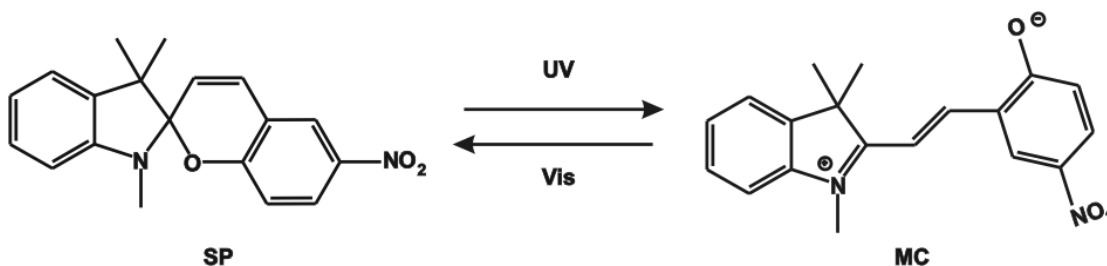


Immobilization of Photo-switchable Spiropyran on Silicon and gold surfaces as Sensor Coatings

Fernando Benito-Lopez, Robert Byrne, Dermot Diamond

CLARITY: The Centre for Sensor Web Technologies, National Centre for Sensor Research (NCSR)

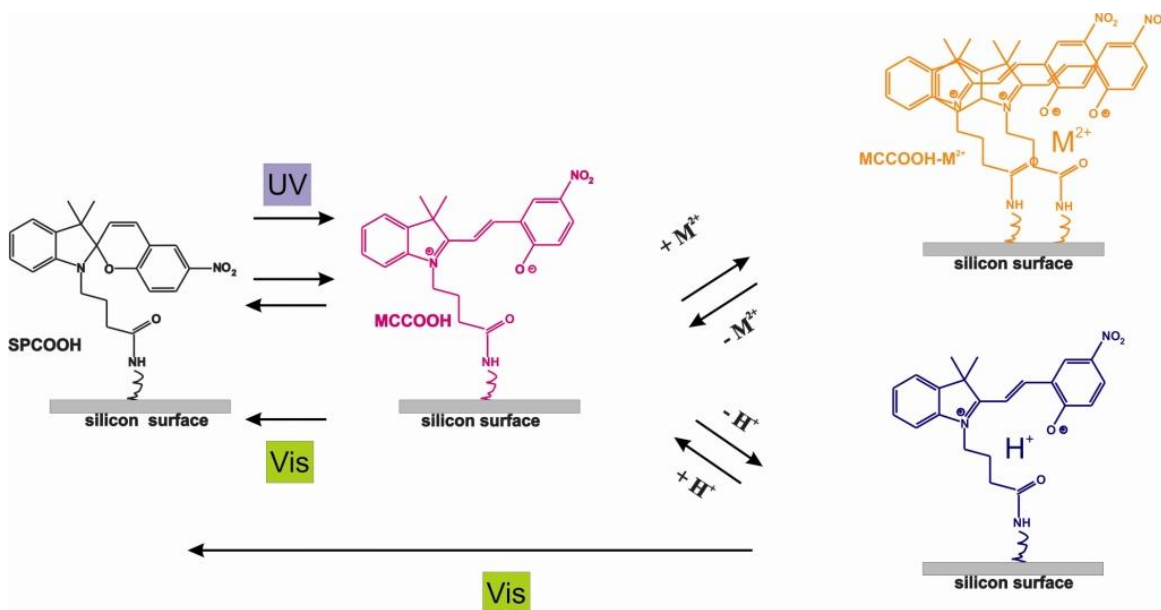
Organic photochromic compounds like spiropyrans are particularly interesting targets for the development of new approaches to sensing since they offer new routes to multifunctional materials that take advantage of their photo-reversible inter-conversion between two thermodynamically stable states (a spiropyran (SP) form, and a merocyanine (MC) form, see scheme 1, which have dramatically different charge, polarity and molecular conformations [1] Furthermore, they can be easily incorporated into surfaces for improving robustness and handling [2-4], but from our perspective, most interesting of all, they have metal ion-binding and molecular recognition properties which are only manifested by the MC form [5]. Based on the coordination-induced photochromism characteristic of the MC form, spiropyrans have been employed as molecular probes for metal ions and organic molecules [6].



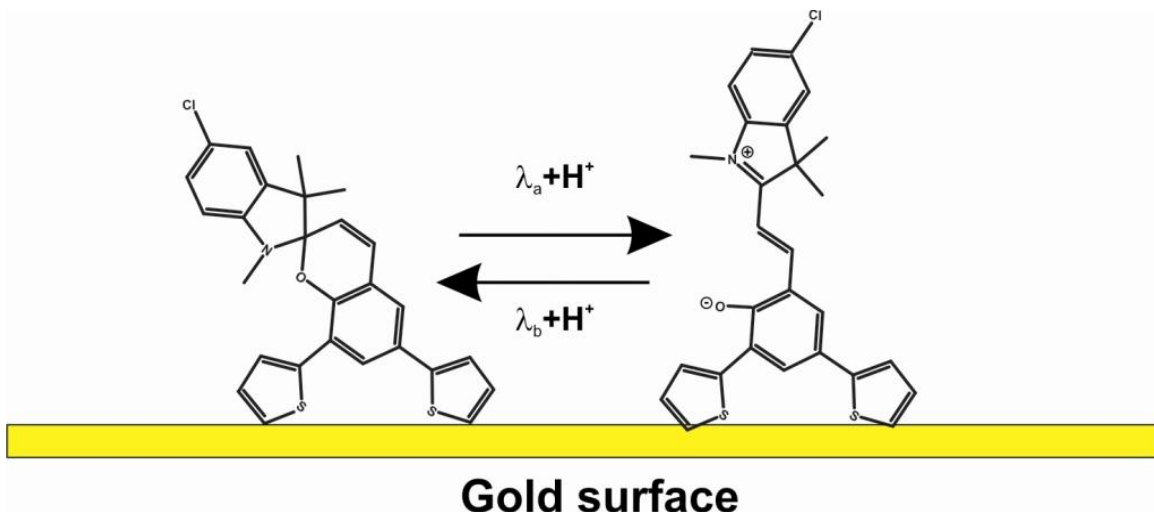
Scheme 1. Structures of spiropyran (closed), left, and merocyanine (open), right.

Aim of the project

The aim of this research will be to investigate the feasibility of the detection of the **photo-reversible inter-conversion** between two thermodynamically stable states of 1'-(3-carboxypropyl)-3,3'-dimethyl-6-nitrospiro-1-benzopyran-2,2'-indoline (Scheme 1) and 1,3,3'-trimethyl-4,5-dithiophene-6-nitrospiro-1-benzopyran-2,2'-indoline SP-S2-Cl (Scheme 2) (a **spiropyran** (SP) form, and a **merocyanine** (MC) form, see scheme 1, which have dramatically different charge, polarity and molecular conformations [6], in **silicon and gold surfaces**. Moreover, these molecules have metal ion-binding and molecular recognition properties which are only manifested by the MC form. **We propose here** the use of the concept of **self assembled monolayer's** in flat surfaces to study the opening/close conformational change of spiropyran molecule (SP \leftrightarrow MC) and its ion-binding properties (MC + $\emptyset \leftrightarrow$ MC- \emptyset). These chemical effects are expected to cause a change in surface wettability; and so, change in surface properties, can be measured by contact angle, SEM and AFM.



Scheme 1: Chemical structure of SP-COOH and MC-COOH and the photoreversible equilibria and metal complexation of the MC-COOH with divalent metal ions, MC-COOH-M²⁺ and protons MC-COOH-H⁺ in a silicon surface.



Scheme 1: Chemical structure of SP-S2-Cl and MC-S2-Cl and the photoreversible equilibria in a gold surface.

Acknowledgements

The project will be carried out with the support of the partner institutions. (i) The Irish Research Council for Science, Engineering and Technology (IRCSET) fellowship number 2089 and Science Foundation Ireland under grant 07/CE/I1147 (CLARITY: The Centre for Sensor Web Technologies)

References

- [1] H. Tian, Y.L. Feng, Next Step of Photochromic Switches? J. Mater. Chem. (2008), 18, 1617-1622.

- [2] A. Radu, S. Scarmagnani, R. Byrne, C. Slater, K.T. Lau, D. Diamond, Photonic Modulation of Surface Properties: A Novel Concept in Chemical Sensing. *J. Phys. D: Appl. Phys.* (2007), 40, 7238-7244.
- [3] S. Scarmagnani, Z. Walsh, C. Slater, N. Alhashimy, B. Paull, M. Macka, D. Diamond, Polystyrene Bead-Based System for Optical Sensing Using Spiropyran Photoswitches. *J. Mater. Chem.* (2008), 18, 5063-5071.
- [4] F. Benito-Lopez, S. Scarmagnani, Z. Walsh, B. Paull, M. Macka, D. Diamond Spiropyran modified PDMS micro-fluidic chip device for photonically controlled sensor array detection of metal ions. ICTBSB-2009, January 26-28, Dublin, Ireland, 43-45.
- [5] Kristen F, Reversible colorimetric ion sensors based on surface initiated polymerization of photochromic polymers. *Chem. Commun.* (2008), 47, 1359-7345.
- [6] M. Inouye, Artificial-Signaling Receptors for Biologically Important Chemical Species. *Coord. Chem. Rev.* (1996), 148, 265-283.