Dual photo- and redox- active molecular switches for smart surfaces
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Summary

Functional surfaces are surfaces that can change their properties in response to specific external stimuli such as light, electrical/redox potential and heat, etc. The response of the surface is obtained by using the monolayers of sensitive molecules (molecular switches) immobilized on the substrates. External stimuli trigger reactions in these compounds manifested in a rotation, isomerization and/or bond breaking-formation, depending on the type of compound. This can be seen macroscopically in changes to surface properties such as light absorption, fluorescence, conductivity, wetting and adhesion. In this dissertation attention is focused on molecular materials that can be addressed with two distinct types of stimuli – light and electrochemical potential.

Molecular behaviour is normally studied in solution initially to identify functionality, where the environmental effects such as intermolecular and molecule-substrate interactions play a minor role. Once the molecular switching in solution is understood, the next step is to immobilize the switch on a metallic substrate as a single molecular layer and to verify that such a monolayer is formed.

Understanding molecular function in monolayers on surfaces is essential for applying molecular switches in molecular electronic devices. Therefore, one of the main goals is to study the functionality of a molecular monolayer on a surface, where the molecules are in a densely packed environment and in proximity to the metallic substrate. Comparison of the molecular behaviour in solution and in a monolayer allows us to understand whether or not the switching function is affected by immobilization on a surface and by interactions with neighbouring molecules.

The state of the art of functional dual responsive (light and redox switchable) compounds is presented in chapter 1. The electrochemical data on photochromic switches in solution and in monolayers shows how several classes of compounds – stilbenes, azobenzenes, dithienylethenes, rotaxanes, spiropyans and bis-thiaxanthylidenes – can be used to develop smart advanced functional surfaces. The overview presented summarizes what has been achieved to date, and what questions remain to be answered; it therefore presents a motivation for several projects that form the basis of this dissertation. Most notably for several types of molecular switches – stilbenes, azobenzenes, dithienylethenes, bis-thiaxanthylidenes and spiropyrans - a redox cycle starting from form A can result in switching to form B, as is achieved by excitation with light. The subsequent chapters of this dissertation show how dual photo- and redox- active bis-thiaxanthylidene and spiropyran can be used to develop functional smart surfaces.

In particular – a bis-thiaxanthylidene, presented in chapter 3, was characterized in solution and has been used in several monolayer applications, however the electrochemistry of the switch in monolayers was not studied in detail before. In brief, four conformational and redox states are accessible in the bis-thiaxanthylidene with light and redox stimuli. One of the conformational states – a twisted state (C) is thermally unstable in solution due to
rapid thermal isomerization to the *syn*-folded (B) and subsequently to the ground *anti*-folded state (A). Immobilization as monolayers on gold and indium tin oxide (ITO) allowed this twisted state to be observed by cyclic voltammetry. On the other hand, the utilization of a redox potential to switch a surface between the neutral (A) and the dicationic (2+) state allowed the hydrophobicity of the surface to be changed reversibly (more than 30° change in water contact angle). The reversible oxidation to the dicationic state was also confirmed with several spectroelectrochemical techniques that provide means of readout of the monolayer’s state for molecular memory applications.

A wide range of techniques are available to study molecular materials. One of them, X-ray photoelectron spectroscopy (XPS) provides information about the oxidation states of the atoms in switchable molecules and affords an estimate of the stoichiometry and thickness of a layer on a substrate. However, how can one be sure that the measured state of the molecular film is not affected by the experimental techniques used to obtain the information? The phenomenon of degradation of monolayers under exposure to X-rays has been demonstrated already several decades ago and is mainly related to the oxidation of the thiolate linker, cleavage of carbon-carbon bonds or desorption from the surface. In chapter 4 the rapid reduction of nitroaromatic groups on bulk roughened gold substrates is described. The reduction process NO$_2$→NO→NOH→NH$_2$ was studied spectroscopically. The reduction can be understood considering the origin of the X-ray damage in alkane thiols – photoelectrons, secondary and inelastically scattered electrons from the metallic (Au, Ag, etc.) substrate travel through the molecular film and interact with S and C atoms leading to oxidation, bond breaking and desorption. Similar processes occur in the case of nitroaromatic monolayers – electrons interact with NO$_2$ groups and in the presence of protons in the ultra-high vacuum chamber reduce nitrogen to lower oxidation states. Polymerization was reported to accompany this process; however the precise assignment based on spectroscopic data of the polymer obtained was not possible. The utilization of substrates such as roughened thin films of gold for monolayer formation allowed for the study of nitroaromatic monolayers and related compounds such as spiropyrans non-destructively.

The photochromism of spiropyran-based molecular switches has been known for more than 60 years. Irradiation of spiropyran with ultraviolet light in solution induces breaking of the central C-O bond of the ring closed spiropyran (SP) and isomerization to the ring-open merocyanine form (MC). It is used in numerous applications ranging from polymeric membranes, drugs and sensors to carbon nanotubes and graphene with photo-controlled properties. To verify whether or not the photochemical switching of spiropyran can occur in a monolayer on gold, the photochromism of self-assembled monolayers (SAM) of spiropyran with a disulfide linker on gold was studied and is reported in chapter 5. The application of multiple spectroscopic techniques to the monolayer formed on gold leads to the conclusion that the initial state of the monolayer is in a spiropyran ring-closed form. The switching to the merocyanine form on the surface with UV light was manifested in
changes in vibrational and electronic properties. Additionally it was possible to drive ring-opening to the MC form with near infrared light in the monolayer. The latter observation has been reported previously for polymers and in solution and is attributed to two-photon absorption by the spiropyrans. Indeed a combination of high cross-section towards the two-photon absorption and a sufficiently intense light source result in near-IR driven switching spiropyran SAMs on gold.

The processes that occur in spiropyrans upon electrochemical oxidation were addressed significantly later in the literature and have received less attention than their photochemistry. It was suggested that the ring-open MC form can be obtained from the ring-closed spiropyran form either photochemically or as a result of electrochemical reduction and oxidation. Irreversible oxidation was thus rationalized by ring-opening and possible dimerization (MC-MC). To establish if the ring opening and dimerization occur upon oxidation of spiropyrans in solution, the oxidation product X was prepared electrochemically on a larger scale and studied spectroscopically. NMR spectroscopy and mass spectrometry of the electrochemically generated X pointed to dimerization of the ring-closed spiropyran form (SP-SP) at the para-position in the indoline moiety, which is in striking contrast to the MC-MC formation proposed in the literature. Additionally, the dimer obtained showed reversible ring-opening to the MC form upon irradiation with UV light to give MC-MC (and possibly SP-MC), as for the monomer. The established mechanism of dimerization was supported by showing that if the active para-position in the indoline aromatic ring is blocked by a methyl group, electrochemical oxidation of the spiropyran becomes reversible.

Monolayers of spiropyran on gold were studied spectroelectrochemically to verify if the dimerization observed in solution occurs also in the SAMs formed on gold. The comparison of electrochemical data in solution and in SAMs showed that oxidation of the spiropyran is fully irreversible with complete formation of the product on the first oxidation cycle. Based on data obtained for the oxidation of SP in solution, spectroscopic data confirmed the formation of dimers. Given that reversible two-electron oxidation of a dimer in a monolayer occurred at lower potentials than those observed for a monomer, the electrochemical sweep to a lower potentials (0.8 V) can be used to read out the state of the spiropyran (monomer/dimer) and an electrochemical sweep to higher potentials (>1V) can be used as 2SP→SP-SP writing functionality. Monocationic and dicationic states can be probed spectroscopically since both have different vibrational and electronic properties. Remarkably, the dimerization on the surface does not block the photochromic functionality of spiropyrans, as was observed in solution and in monolayers of the monomer by XPS and Raman spectroscopies. Therefore, a device with a photo- and redox-active “write” and electrochemical and spectroscopic “read” functions can be developed.