Monitoring chemical reactions and identifying the compounds formed both during (as intermediates) and at the end of a reaction (products) is one of the central pillars of contemporary molecular chemistry. Gathering information on these aspects is not only important for reactions in solution (or gas-phase), but also for reactions that take place in the solid state, and at the interface between states (for example, gas-solid interfaces). This last situation, reactions at interfaces, is especially significant in understanding heterogeneous reactions that are at the basis of the large number of industrial chemical processes. The key (catalytic) reactions in many of these large-scale processes occur at the surface of solids, such as metals, minerals and composite materials.

Whereas reactions in solution were the major focus of molecular chemistry, in the second half of the twentieth century it became more and more possible to follow reactions occurring at the interface of phases. Systems consisting of a combination of solid materials and molecular compounds are of interest in the studies described in this thesis, especially so-called self-assembled monolayers (SAMs). These self-assembled systems, in which the molecules form molecular aggregates as they assemble on a suitable surface (usually aided by the formation of bonds between the molecules and the surface, so-called adsorption), were developed (or rather: discovered) in earnest in the 1980s, and the research field has expanded rapidly since. This field of study is particularly special, since it draws scientists from a diverse range of backgrounds together, in efforts to create and study such interfaces, as well as discover potential uses for these new materials. An example of a real-world application of adsorbed compounds on surfaces is the formation of protective monolayers on metals that prevent otherwise rapid oxidation (rust/corrosion).

One of the reasons why molecules adsorbed on gold surfaces are a focus point of this thesis is that these surfaces have specific properties which means they can be studied by powerful spectroscopic techniques based on enhancement of the phenomenon Raman scattering, so-called surface-enhanced Raman scattering (SERS), which was discovered by accident in the middle of the last century already. This type of spectroscopy reports vibrational information of molecules - that is, it provides information on the vibrations of bonds between atoms, and the powerful feature of SERS, as an enhanced form of Raman spectroscopy, is that it allows for the determination of the composition (structure) of tiny amounts present on the surface, provided that the molecules are close by (within roughly a nanometer).

In Chapter 2, the relation between pH and electrode potential is a central point. We noticed that the SERS spectrum of a simple molecule – thiophenol – adsorbed on a gold electrode changes when applying an electrical potential of that at which water can be oxidised (to oxygen and protons), in the same way as it does by a change in pH.
Since the vibrational spectrum is directly related to its molecular structure, it can be concluded that both the application of a sufficiently positive electrode potential and the addition of acid cause the same change in molecular structure of adsorbed thiophenol. The precise origin of the structural change is unfortunately highly challenging to pinpoint exactly, but we obtained a strong indication from calculations (simulations) of thiophenol-gold structures that it involves the orientation of the molecule with respect to the gold surface. The non-innocence of electrochemistry, by applying an electrode potential to a solution or material, is shown also in Chapter 3 to have the potential to result in unexpected and/or undesired reactions.

The bulk of the work in this thesis focuses on a family of organic compounds that have fascinated organic chemists for decades: the spiropyrans. Spiropyrans are well-known as multi-responsive molecular switches because they can be switched between their so-called open and closed molecular structures, the spiropyran and the merocyanine isomers, by heat, light, pH, ionic strength, and electrical potential.

In Chapter 3, we study the redox chemistry of a spiropyran designed to be reversibly oxidisable (loose an electron) and reducible (gain an electron) without undergoing a subsequent chemical reaction - at least, that was the intention, and this property was indeed conserved as long as the molecules did not stay close to the electrode for long. Instead, molecules self-assembled in a monolayer on a surface, that doubles as electrode, are exposed to a significantly lower pH than farther from the electrode surface, when the applied electrode potential is such that oxidation of water to oxygen and protons is possible. This chapter details our study of the protonation of these spiropyrans during electrochemical measurements (for example, cyclic voltammetry) with, amongst a variety of other techniques, SERS spectroscopy, in our quest to find out which of the protonated merocyanine isomers are actually formed.

The latter type of stimulus mentioned above for triggering molecular switching of spiropyrans, electrical potential, is central to the work described in Chapters 4 and 5, in which we show for the first time that a suitably decorated (substituted) spiropyran can be repeatedly switched between its closed and open structure using electrochemical stimulation.

The removal of an electron (oxidation) from the closed isomer results in a destabilisation of that molecular structure and the consequent spontaneous breaking of a bond between an oxygen and a carbon atom in the molecule. This leads to the formation of the open (merocyanine) isomer (still with one electron less than in its normal state), which can then, in turn, pick up an electron (reduction) to acquire a neutral state. This molecular structure is also unstable, therefore the previously broken carbon-oxygen bond reforms and the original spiropyran structure is regained.

In Chapter 4, we have extensively described the redox switching, by means of an oxidation-reduction cycle, of the ditertbutyl-substituted spiropyran in solution. In Chapter 5, we show that this method of molecular switching also works for spiropyrans (with the same substitution pattern) bound to a gold surface. As mentioned above, the advantage of these self-assembled monolayers on an electrode is that the change in molecular structure during a redox cycle can be followed by SERS spectroscopy. In preparation of these future experiments, we have characterised the different iso-
Redox switching of a ditertbutyl-substituted spiropyran with the four compounds depicted that are involved in the cycle (from Chapter 4): spiropyran and merocyanine in neutral and oxidised state.

Although the study of fundamental properties of single layers of molecules on gold under various conditions, mainly the influence of pH and electrode potential, is the focus of this thesis, a side-step into the field of inorganic catalysis is made in the last (but chronologically the first) chapter of this thesis. However, as with earlier chapters, the role of protons comes back again in Chapter 6, when studying the effect of Lewis acids on transition metal catalysis, more specifically using a manganese oxidation catalyst. We demonstrate that the role of Lewis acids such as scandium(III) triflates, earlier (and erroneously) ascribed as binding to the catalyst, boils down to the liberation of Brønsted acids (protons) due to undergoing hydrolysis. And indeed, the activation of the manganese catalyst could be reproduced using strong Brønsted acids as additives in place of Lewis acids.