Reversible conductance and surface polarity switching with synthetic molecular switches

Kumar, Sumit

DOI:
10.33612/diss.95753670

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Switching surfaces, also called smart surfaces, can change their properties in response to external stimuli such as light, electrical potential, pH and heat. The transformation of an ordinary surface into a smart surface can be achieved by functionalization of a parent surface (substrate) with functional molecules. In this dissertation photoresponsive smart surfaces were obtained by immobilizing monolayers of light active molecules (molecular switches) on the substrate. Light as external stimulus triggers reactions in these molecules, which, depending on the specific molecule, induce rotation, isomerization and/or bond breaking. These changes influence the surface properties, such as light absorption, fluorescence, conductivity, wetting and adhesion.

We proceeded through three basic steps: first the molecules were studied in solution where they have more degrees of freedom. Their switching behaviour was investigated and the reversibility of the switching during multiple back and forth switching cycles was studied. Once the molecular switching in solution was understood, the next step was to immobilize the switches on a metallic substrate in the form of a single molecular layer, to check that a monolayer is indeed formed and to characterize the properties of the molecules in the self-assembled monolayer (SAM) as well as of the surface as a whole. In other words, the goal of the second step was to study the functionality of the molecular monolayer on a surface, where the molecules are densely packed and in proximity of the metallic substrate. Comparison of the molecular behaviour in solution and in a monolayer allowed us to understand whether or not the switching function was affected by surface immobilization and by interactions with neighbouring molecules. When the properties of these molecules were well understood and optimized on metallic surfaces, the last step was to develop an electronic device. In this thesis we used monolayers of molecular switches to make a memory device, which is able to encode information on the surface.

The state of the art of conductivity switching for light responsive molecules is presented in Chapter 3. We successfully fabricated a monolayer spiropyran switches between two electrodes and demonstrated a change in conductivity of the SAM light induces the ring-closed form of spiropyran (SP) to convert into the ring-open merocyanine form (MC) by photoisomerization. Spiropyran monolayers were found to undergo also secondary reactions during the switching cycle due to the steric congestion on the gold surface. To solve this problem we developed a protocol to assemble a mixed monolayer where the spiropyrans are separated by 1 hexanethiol molecules. We observed an increase in the magnitude of conductance switching, from a factor of 8 in pristine SAMs to 35 in mixed monolayer (mixed SAMs), accompanied by a decrease in fatigue when repeatedly switching $\text{SP} \rightarrow \text{MC} \rightarrow \text{SP}$. We attributed the superior performance of the mixed SAMs to an optimized packing of the spiropyrans at the electrode interface.

In Chapter 4, a photochemical nonvolatile memory device is described. The
integrity of the molecules in the device was verified by X-ray photoelectron spectroscopy (XPS). Locking of the spiropyrans in the MCH$^+$ form by acid is well studied in solution. We successfully translated this methodology to metallic electrodes, showing for the first time that mixed monolayers of spiropyran can be locked in a high-conductance state by forming MCH$^+$ on the surface. This process circumvents the spontaneous relaxation of MC back to SP, which we exploited optically switchable, non-volatile memory device. We showed that exposure to acid, base, light and applied bias does not damage the monolayers nor promote any side reactions, meaning that there is no fundamental limit to the reversibility of the process. We demonstrated reading, writing, erasing, re-writing and re-reading six bytes (48 bits) in simple, soft punch card devices, and thereby provided the proof-of-concept for future devices, which could be miniaturized using arrays of nanoscale tips to couple in the light.

For the work in Chapter 3, we used molecules comprising a five membered ring with a disulphide bond ($S–S$) for surface grafting. We observed that the conductivity was lower for pure spiropyran monolayers having multiple sulfur species as anchoring groups than for mixed SAMs of molecules that bind with a single Au–S bond. Therefore, in Chapter 5 we investigated the $S–S$ bond on the gold surface and its effect on conductivity measurements when used as an anchoring moiety. For this purpose, we used derivatives of (+$\alpha$)-lipoic acid of different lengths, for which we could deduce the transmission coefficient ($\beta$) and injection current density. The thickness measurements by XPS and an unusual $\beta$ value (0.01 Å$^{-1}$) indicated that pure monolayers were poorly ordered on the surface. For mixed monolayers, the $\beta$ value (0.53 Å$^{-1}$) confirmed that molecules were better packed on the gold surface. Moreover, differences in the injection current density of mixed and pure SAMs also corroborate that the coupling of Au–S bonds can affect the conductivity.

The last topic treated in this dissertation concerns not conductance switching but surface polarity switching, with the help of a heteroternary photoswitchable complex immobilized on a substrate. We employed one of the largest macrocyclic hosts, cucubit[8]uril (CB[8]), which can simultaneously accommodate up to two guest molecules within its hydrophobic cavity, in particular an electron poor paraquat (MV$^{2+}$) and electron rich E-azobenzenes. In Chapter 6, we present a simple design of a novel CB[8] guest comprising a cationic azobenzene photoswitch and a MV$^{2+}$ moiety connected with a tetraethyleneglycol to a thiol anchoring group for surface modification. The E-azobenzenes switches on the surface can be efficiently functionalized with CB[8], and the complex shows a clear switching behaviour under UV irradiation, which results in a water contact angle change of 20°. Such a large photoswitchable wettability allows for establishing local surface tension gradients by light and opens a door for the use of these surfaces in Lab-on-chip technology.