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Mahmut Deniz Yilmaz

Orthogonal Supramolecular Interaction Motifs for Functional Monolayer Architectures

Doctoral Thesis accepted by
the University of Twente, The Netherlands

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ISSN 2190-5053

ISSN 2190-5061 (electronic)

ISBN 978-3-642-30256-5

ISBN 978-3-642-30257-2 (eBook)

DOI 10.1007/978-3-642-30257-2

Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2012938867

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Printed on acid-free paper

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Parts of this thesis have been published in the following journal articles:

1. T. Gang, **M. Deniz Yilmaz**, D. Ataç, S. K. Bose, E. Strambini, A. H. Velders, M. P. de Jong, J. Huskens, W. G. van der Wiel, *Nature Nanotechnology*, DOI: 10.1038/NNANO.2012.1. “Tunable Molecular Spin Doping of a Metal”
2. B. Eker, **M. Deniz Yilmaz**, S. Schlautmann, J. G. E. Gardeniers, J. Huskens, *International Journal of Molecular Science* **2011**, 12 (11), 7335–7351. “A Supramolecular Sensing Platform for Phosphate Anions and an Anthrax Biomarker in a Microfluidic Device”
3. W. P. Voorthuijzen, **M. Deniz Yilmaz**, W. Naber, J. Huskens, Wilfred Van der Wiel, *Advanced Materials*, **2011**, 23 (11), 1346–1350. “Local doping of silicon using nanoimprint lithography and molecular monolayers”
4. W. P. Voorthuijzen, **M. Deniz Yilmaz**, A. Gomez-Casado, P. Jonkheijm, W. G. van der Wiel, J. Huskens, *Langmuir*, **2010**, 26 (17), 14210–14215. “Direct patterning of covalent organic monolayers on silicon using nanoimprint lithography”
5. **M. Deniz Yilmaz**, S. H. Hsu, D. N. Reinhoudt, A. H. Velders, J. Huskens, *Angewandte Chemie International Edition*, **2010**, 49, 5938–5941. “Ratiometric fluorescent detection of an anthrax biomarker at molecular printboards”
6. S. H. Hsu, **M. Deniz Yilmaz**, C. Blum, V. Subramaniam, D. N. Reinhoudt, A. H. Velders, J. Huskens, *Journal of the American Chemical Society*, **2009**, 131, 12567–12569. “Expression of Sensitized Eu^{3+} Luminescence at a Multivalent Interface”

*To my wife, grandma, parents and all my
family*

Supervisor's Foreword

Multivalency is the phenomenon that describes the interaction between multivalent receptors and multivalent ligands. It is well known to play a pivotal role in biochemistry, particularly in protein–carbohydrate interactions, both in solution and at interfaces (e.g. for the infection of cells by the attachment of viruses or bacteria to cell membranes). In particular in the latter case, multivalency is often poorly understood in a quantitative sense.

Supramolecular host–guest chemistry has been well established in solution, but its use at interfaces remains limited to for example sensor development for specific guest compounds. In order to *build* assemblies at surfaces through supramolecular interactions for nanotechnological applications, other demands have to be met, such as larger thermodynamic and kinetic stabilities of the assemblies. For many supramolecular motifs, this inevitably leads to the use of *multivalent* interactions.

The main line of this thesis deals with *heterotropic* multivalency, which is the use of *multiple* interaction motifs. After a thorough introduction ([Chap. 2](#)) into orthogonal interactions to create monolayer architectures, the first three chapters deal with the bottom-up development of a platform based on such orthogonal host–guest and metal–ligand coordination interactions ([Chap. 3](#)) and its application in a novel, sensitive and exciting anthrax sensor platform ([Chap. 4](#)) and a microfluidic sensor for biological anions ([Chap. 5](#)).

[Chapters 6](#) and [7](#) deal with other forms of molecular monolayers in the development of nanoelectronic and spintronic devices. This thesis provides a colorful illustration of the current powers of nanochemistry, and in particular of monolayers in the development of functional interfaces for biosensing and nanotechnology. The results described in this thesis have provided a boost to ongoing and new projects within the group and MESA+ on nanoelectronics, surface gradients and electrochemical and fluorometric biosensing. A true piece of exciting science at the forefront of nanochemistry! Enjoy!

Jurriaan Huskens

Acknowledgments

Finally I finished my PhD thesis, and I would like to thank many people for their help and support during these four years. I am very proud that now it is time to write the most important part of the thesis. It is not easy to summarize my all acknowledgments in a few words, but just I can say that I am really grateful to all people I met during my PhD.

My first acknowledgment goes to my promoter and supervisor, Jurriaan Huskens. Actually I don't know where I will start and I will never find enough words to say. I thank you for accepting me as a PhD student and to be part of this group. I will never forget our biweekly meetings, where I have learnt so much from you. During these meetings you always gave me lot of confidence, encouragement and freedom mostly when I lost my way. You were always patient to listen to me when I brought completely different ideas while proceeding a certain project. I want to thank you for all your help, ideas, guidance, and patience throughout this whole period. Thank you very much for everything you did for me.

I would like to thank to Aldrik and Wilfred for the meetings we had in the last 3 years of my PhD and for the scientific contribution. They were very useful with a lot of nice ideas. I really enjoyed and learned so many things during our meetings.

During these four years I had the chance to collaborate with many people, the results of which are presented in this thesis. I owe my appreciation to Shu-Han Hsu for all her help. You always had time for me to help me to prepare the patterned samples and for discussions on results. We had many nice discussions which were very essential to obtain results presented in [Chaps. 3](#) and [4](#). I would like to thank Dr. Bilge Eker for introducing me to the world of microchips and for her participation to [Chap. 5](#). I really learnt a lot from you. I would like to thank Pim for his contribution to [Chap. 6](#). You were my first master student and I couldn't support you much during your studies due to my lack of knowledge about nanoimprint lithography. At the end, when we looked through the results, we managed this project successfully. My appreciation also goes to Wouter Naber and Peter Tijssen for their help for [Chap. 7](#). It was a long project and still continues with a new PhD student, Derya. I hope you will complete this project during your PhD. I would like

thank all of you again, it was a pleasure to work with you and without your help I could not have completed my PhD. My special thanks go to Mudassir Iqbal. Dear Mudooo, thank you very much for all your friendship and help during these years. I will never forget our discussions the topic could be whatever. I appreciate your friendship. I would like to thank Marcel and Richard for their technical support. The secretaries of MnF/SMCT/BNT, Izabel and Nicole, are also thanked for taking care of all administrative works. I thank you Melissa for going so carefully through my concept thesis. I also spent some time doing EPR measurements in Barcelona. Dear Veronica, thanks for your help and contribution on EPR experiments. I really enjoyed my short trip to Barcelona. I would like to thank Tom. Dear Tom, thank you very much for your great effort to translate my thesis summary from English to Dutch. I appreciate your kindness. I would like to thank Janet Acikgoz. Dear Janet, thanks for encouraging me in the first year of PhD. Whenever I was upset, you tried to help me recover again and again.

During my PhD, I have had opportunity to meet a lot of fantastic people, Xing Yi, Duan, Henk, Sachin, Veera, Elisabetta, Riccardo, Francesca, Ignacio, Andras, Huaping, Yiping, Srinidhi, Tian, Kim, Roberto, Albert, Arancha, Carmen, Sven, Carlo, Jordi, Lanti, Jealemy, Pieter, Alberto, Melanie, Raluca, Vijay, Chien-Ching Wu, Dae June, Oktay, Erhan, Serkan, Mine, Anna, Rajesh, Nicolai, and many more. All the people I mentioned here have contributed to make the time I spent in Enschede an unforgettable time of my life. But most importantly, I owe my deepest gratitude to my family; my parents, my two brothers for all the support they give me. Canim annem, babam, kardeslerim. Sizlerin sevgi ve anlayisiyla ben bu doktorayi bitiriyorum. Bana desteklerinizi hicbir zaman eksik etmediniz. Sizleri cok ama cok seviyorum.

Lastly, this thesis is dedicated to the owner of my heart, Burcu, I wouldn't have completed this thesis without you. You are my soul, my lover, and my best friend. My heart is filled with your love. We have overcome all bad moments, and welcome every good moments hand-in-hand in our life. We are growing and walking together to our future. I love you! Seni cok seviyorum askim herseyim.

This research has been financially supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO-CW), (grant 700.55.029 to Jurriaan Huskens). The research was carried out within the Molecular Nanofabrication (MnF) group, MESA⁺ Institute for Nanotechnology, University of Twente, The Netherlands.

Enschede, The Netherlands, May 2011

Mahmut Deniz Yilmaz

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Summary

The research described in this thesis is focused on the combination of orthogonal supramolecular interactions for functional monolayer architectures on surfaces. The term “orthogonal supramolecular interactions” refers to non-covalent interactions that do not influence each other’s assembly properties when applied in the same system. Orthogonal self-assembly allows extended control over the self-assembly process and promotes new materials properties. Individual noncovalent interactions (e.g. hydrogen bonding, metal coordination, electrostatic or host–guest interactions) have been employed in many studies. However, the combination of different supramolecular interactions in the same system can improve the properties of the materials. The research described in this thesis aims to develop hybrid, multifunctional monolayers by using orthogonal supramolecular interactions, enabling the control over the monolayer composition and functionality. Orthogonal host–guest and lanthanide–ligand coordination interaction motifs have been employed to create supramolecular luminescent monolayers in the first part of the thesis (Chaps. 3–5). The second part of the thesis (Chaps. 6 and 7) deals with the fabrication of functional monolayers on silicon and gold substrates for applications in electronics.

A general introduction has been given in Chap. 1 which addresses the importance of non-covalent interactions for the fabrication of functional surfaces.

A literature overview has been given in Chap. 2 on the use of supramolecular interactions for the generation of hybrid assemblies and materials. Supramolecular chemistry and molecular self-assembly including hydrogen bonding, metal coordination, electrostatic and host–guest interactions to direct the immobilization of functional systems on surfaces are discussed in detail. Special attention is given to the combination of different supramolecular interaction types for the generation of functional monolayer architectures.

Chapter 3 describes the assembly of a guest-functionalized naphthalene antenna and a Eu^{3+} -complexed EDTA-based ligand molecule onto a receptor surface by combining the orthogonal host–guest and metal–ligand coordination motifs. Local fluorescence emission spectra of the immobilized complex demonstrated the

occurrence of sensitized Eu^{3+} luminescence. The energy transfer efficiency between the antenna and the Eu^{3+} complex was determined by time-resolved fluorescence measurements and found to be about 35 %. The stoichiometry of complexation between antenna and Eu^{3+} complex was investigated by the very first Job plot analysis at a surface and found to be 1:1 by examining the sensitized luminescence of the surface-immobilized complex at different antenna- Eu^{3+} complex ratios.

In **Chap. 4**, the same lanthanide complex system was used for the ratiometric detection of dipicolinic acid (DPA), which is a unique biomarker for anthrax bacterial spores, with high sensitivity and selectivity on a supramolecular monolayer surface. The fluorescence intensity ratio of the lanthanide-based surface receptor system upon addition of different concentrations of DPA showed that the recovery of the naphthalene emission is practically complete in the presence of only 200 nM DPA. The intensity ratio of the Eu^{3+} -based sensing platform as a function of time upon addition of 200 nM DPA indicated that the sensing response is complete within 10 min. The detection limit of the system was also investigated and found to be about 25 nM of DPA. To exhibit the selectivity of the supramolecular sensing surface, fluorescence changes upon addition of different competitive aromatic ligands were investigated. The negligible changes demonstrated the excellent selectivity of the system for DPA.

Chapter 5 has introduced a supramolecular sensing platform on a microchip surface that allows the detection of biologically relevant phosphate anions and aromatic carboxylic acids in a high-throughput format. The Eu^{3+} -based supramolecular sensing system was implemented on the surface of a multichannel chip. The sensing layer on the microchip surface is an ensemble of the antenna and Eu^{3+} -complexed ligand. When an anionic guest was added to the ensemble, it displaced the antenna, and triggered a fluorescence decrease upon binding to the Eu^{3+} center. ATP and pyrophosphate among various phosphate anions, and the anthrax biomarker DPA among various aromatic carboxylic acids showed a strong response to the sensitized Eu^{3+} luminescence-based microchip surface.

Chapter 6 describes the local doping of oxide-free silicon using nanoimprint lithography (NIL) and molecular monolayers. Covalently bonded Si-C monolayer patterns with feature sizes ranging from 100 nm to 100 μm were created via a local hydrosilylation reaction on NIL-patterned resist areas. These patterns were characterized by XPS, AFM, and TOF-SIMS measurements. Monolayer patterns with 100 μm features were fabricated to enable pattern characterization by XPS. Elemental mapping spectra showed that the patterned monolayers were created by hydrosilylation. To fabricate the nanoscale features, a nickel-plated mold containing a square array of 150 nm pillars was used and the resulting structures were visualized by AFM. Results showed that clearly defined patterns were obtained. Using a phosphorus-containing organic precursor, highly-doped and patterned (μm scale) regions in nearly intrinsic silicon were successfully fabricated. These patterned regions were characterized by TOF-SIMS for imaging and depth profiling. The dopant surface dose on a doped area measured $(2.3 \pm 0.1) \times 10^{19}$ P atoms. cm^{-3} corresponding to an areal dose on a doped area of $5.6 \pm 0.1 \times 10^{13}$ P

atoms.cm⁻². Electrical characterizations were performed by Hall and sheet-resistance measurements. An average sheet carrier density was determined and found to be $1.9 \pm 0.1 \times 10^{13}$ cm⁻² at 300 K and $9.4 \pm 0.1 \times 10^{12}$ cm⁻² at 150 K in case of patterned samples. More importantly, the resistance measured on line-patterned substrates along the line direction was significantly lower than when measured perpendicular to the pattern direction.

Chapter 7 describes the fabrication of monolayers of organic molecules with unpaired spins on a thin gold film. Nitroxyl 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radicals and terpyridinyl-cobalt complexes were used in this study. The existence of unpaired spins in self-assembled monolayers was investigated by XPS, and CV measurements. XPS measurements identified the cobalt ions in the monolayer. The two main peaks occurred at 781.3 and 796.3 eV, corresponding to the Co2p_{3/2} and Co2p_{1/2} states, respectively. The CVs of cobalt complexes on gold substrate showed a typical reversible electrochemical reaction, with an oxidation peak at 0.22 V corresponding to the Co^{3+/2+} process. The CVs of TEMPO radicals exhibited a symmetrical reversible one electron redox process. The redox potentials were +0.72 V and +0.68 V versus Ag/AgCl, respectively. Electrical transport measurements of terpyridinyl-cobalt complexes showed an increase of the sheet resistance of gold layers covered with a SAM of magnetic and non-magnetic molecules when the temperature was decreased. Electrical transport measurements of TEMPO radicals were carried out and no significant difference in resistance between the bare gold and the gold covered with the monolayer was observed.

The results presented in this thesis illustrate the power of relatively weak supramolecular interactions to direct the immobilization of functional systems on surfaces. The work on the combination of host-guest and lanthanide-ligand coordination interaction motifs on surfaces demonstrates that hybrid, multifunctional supramolecular monolayers can be fabricated by integrating different non-covalent interactions in the same system. Hence, the combination of different supramolecular interactions opens up new avenues for the fabrication of complex hybrid organic-inorganic materials and stimuli-responsive surfaces.