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Mahmut Deniz Yilmaz

Orthogonal Supramolecular Interaction Motifs for Functional Monolayer Architectures

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Orthogonal Supramolecular Interaction Motifs for Functional Monolayer Architectures

Doctoral Thesis accepted by
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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"

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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 achitectures, 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.

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Enschede, The Netherlands, May 2011 Mahmut Deniz Yilmaz

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