

# Contents

|                                                                                                            |    |
|------------------------------------------------------------------------------------------------------------|----|
| <b>1 General Introduction</b> . . . . .                                                                    | 1  |
| References . . . . .                                                                                       | 2  |
| <b>2 Orthogonal Supramolecular Interaction Motifs<br/>for Functional Monolayer Architectures</b> . . . . . | 3  |
| 2.1 Introduction . . . . .                                                                                 | 3  |
| 2.2 Hydrogen Bonding Directed Assembly on Surfaces . . . . .                                               | 4  |
| 2.2.1 Assembly of Molecules on SAMs . . . . .                                                              | 4  |
| 2.2.2 Assembly of Nanoparticles on SAMs . . . . .                                                          | 6  |
| 2.3 Metal Coordination Directed Assembly . . . . .                                                         | 7  |
| 2.3.1 Assembly of Molecules on SAMs . . . . .                                                              | 7  |
| 2.3.2 Assembly of Nanoparticles on SAMs . . . . .                                                          | 8  |
| 2.3.3 Assembly by Electrostatic Interactions . . . . .                                                     | 10 |
| 2.3.4 Assembly of Molecules on SAMs . . . . .                                                              | 11 |
| 2.3.5 Assembly by Host–Guest Interactions . . . . .                                                        | 13 |
| 2.3.6 Assembly of Molecules on SAMs . . . . .                                                              | 13 |
| 2.4 Combination of Different Orthogonal Supramolecular<br>Interaction Motifs . . . . .                     | 15 |
| 2.5 Conclusions . . . . .                                                                                  | 22 |
| References . . . . .                                                                                       | 23 |
| <b>3 Expression of Sensitized Eu<sup>3+</sup> Luminescence<br/>at a Multivalent Interface.</b> . . . . .   | 27 |
| 3.1 Introduction . . . . .                                                                                 | 27 |
| 3.2 Results and Discussion . . . . .                                                                       | 28 |
| 3.2.1 Synthesis . . . . .                                                                                  | 28 |
| 3.2.2 Complex Formation in Solution . . . . .                                                              | 29 |
| 3.2.3 Complex Formation at the Molecular Printboard . . . . .                                              | 31 |
| 3.3 Conclusions . . . . .                                                                                  | 35 |

|          |                                                                                                         |           |
|----------|---------------------------------------------------------------------------------------------------------|-----------|
| 3.4      | Experimental Section . . . . .                                                                          | 36        |
| 3.4.1    | General Procedures . . . . .                                                                            | 36        |
| 3.4.2    | EDTA-Based Tetraethylene Glycol Adamantyl<br>Ether Dimer 1 . . . . .                                    | 36        |
| 3.4.3    | Eu <sup>3+</sup> Complex of 1 . . . . .                                                                 | 37        |
| 3.4.4    | 1-Naphthoic Acid-6-(3, 5-Di(Tetraethylene Glycol<br>Adamantyl Ether) Benzyl Ether 2 . . . . .           | 37        |
| 3.4.5    | EDTA-Based Tetraethylene Glycol Dimer 3 . . . . .                                                       | 38        |
| 3.4.6    | Eu <sup>3+</sup> Complex of 3 . . . . .                                                                 | 38        |
| 3.4.7    | 1-Naphthalene sulfonic acid-6-(3, 5-di(tetraethylene<br>glycol adamantyl ether) benzyl ether 4. . . . . | 38        |
| 3.4.8    | 3, 5-Bis(Tetraethylene Glycol Adamantyl Ether)<br>Benzyl Alcohol 5 . . . . .                            | 38        |
| 3.4.9    | 3, 5-Bis(Tetraethylene Glycol Adamantyl Ether)<br>Benzyl Bromide 6 . . . . .                            | 39        |
| 3.4.10   | Substrate and Monolayer Preparation . . . . .                                                           | 39        |
| 3.4.11   | Microcontact Printing. . . . .                                                                          | 40        |
| 3.4.12   | Printing of 1 and 2 (or 4), Followed<br>by EuCl <sub>3</sub> Immersion . . . . .                        | 40        |
| 3.4.13   | Printing of 2, Followed by 1.Eu <sup>3+</sup><br>(or 3.Eu <sup>3+</sup> ) Immersion . . . . .           | 40        |
| 3.4.14   | Printing of Different Ratios of 1 and 2, Followed<br>by EuCl <sub>3</sub> Immersion . . . . .           | 41        |
| 3.4.15   | Time-Resolved Fluorescence Measurements . . . . .                                                       | 41        |
| 3.4.16   | Fluorescence Microscopy . . . . .                                                                       | 41        |
| 3.4.17   | Fluorescence Spectral Microscopy . . . . .                                                              | 41        |
| 3.4.18   | Fluorescence Lifetime Spectrophotometry. . . . .                                                        | 42        |
|          | References . . . . .                                                                                    | 42        |
| <b>4</b> | <b>Ratiometric Fluorescent Detection of an Anthrax Biomarker<br/>at Molecular Printboards . . . . .</b> | <b>45</b> |
| 4.1      | Introduction . . . . .                                                                                  | 45        |
| 4.2      | Results and Discussion. . . . .                                                                         | 46        |
| 4.3      | Conclusions . . . . .                                                                                   | 50        |
| 4.4      | Experimental Section . . . . .                                                                          | 51        |
| 4.4.1    | Materials . . . . .                                                                                     | 51        |
| 4.4.2    | Substrate and Monolayer Preparation . . . . .                                                           | 53        |
| 4.4.3    | Microcontact Printing. . . . .                                                                          | 53        |
| 4.4.4    | Fabrication of the Sensing Platform<br>and DPA Detection . . . . .                                      | 54        |
| 4.4.5    | Fluorescence Microscopy . . . . .                                                                       | 54        |
|          | References . . . . .                                                                                    | 55        |

|          |                                                                                                    |            |
|----------|----------------------------------------------------------------------------------------------------|------------|
| <b>5</b> | <b>A Supramolecular Sensing Platform in a Microfluidic Chip. . . . .</b>                           | <b>57</b>  |
| 5.1      | Introduction . . . . .                                                                             | 57         |
| 5.2      | Results and Discussion. . . . .                                                                    | 59         |
| 5.2.1    | Fabrication of the Sensing Platform<br>and Anion Detection . . . . .                               | 59         |
| 5.2.2    | Sensing of Biologically Relevant Phosphates . . . . .                                              | 61         |
| 5.2.3    | Screening of an Anthrax Biomarker and Potentially<br>Interfering Anions . . . . .                  | 64         |
| 5.3      | Conclusion . . . . .                                                                               | 66         |
| 5.4      | Experimental Section . . . . .                                                                     | 67         |
|          | References . . . . .                                                                               | 68         |
| <b>6</b> | <b>Local Doping of Silicon Using Nanoimprint Lithography<br/>and Molecular Monolayers. . . . .</b> | <b>71</b>  |
| 6.1      | Introduction . . . . .                                                                             | 71         |
| 6.2      | Results and Discussion. . . . .                                                                    | 73         |
| 6.2.1    | NIL-Patterned Monolayers on Silicon . . . . .                                                      | 73         |
| 6.2.2    | Local Doping of Silicon by NIL-Patterning,<br>Monolayer Formation and RTA. . . . .                 | 79         |
| 6.3      | Conclusions . . . . .                                                                              | 84         |
| 6.4      | Experimental Section . . . . .                                                                     | 85         |
|          | References . . . . .                                                                               | 89         |
| <b>7</b> | <b>Fabrication of Two-Dimensional Organic Spin<br/>Systems on Gold . . . . .</b>                   | <b>91</b>  |
| 7.1      | Introduction . . . . .                                                                             | 91         |
| 7.2      | Result and Discussion . . . . .                                                                    | 93         |
| 7.2.1    | Monolayer Fabrication and Characterization . . . . .                                               | 93         |
| 7.2.2    | Electrical Characterization . . . . .                                                              | 93         |
| 7.3      | Conclusion . . . . .                                                                               | 97         |
| 7.4      | Experimental Section . . . . .                                                                     | 98         |
|          | References . . . . .                                                                               | 99         |
|          | <b>About the Author . . . . .</b>                                                                  | <b>101</b> |