

University of Groningen

Surface Engineering for Molecular Electronics

Qiu, Xinkai

DOI:
[10.33612/diss.146270150](https://doi.org/10.33612/diss.146270150)

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:
2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Qiu, X. (2020). *Surface Engineering for Molecular Electronics*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.146270150>

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).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

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.

Surface Engineering for Molecular Electronics

Xinkai Qiu



**university of
 groningen**

**faculty of science
 and engineering**

**stratingh institute
 for chemistry**

The work described in this thesis was performed in the research group Chemistry of Molecular Materials and Devices of the Stratingh Institute for Chemistry at the University of Groningen, the Netherlands.

Cover design: Xinkai Qiu

Cover image: An illustration of the charge transport through the self-assembled bilayers of triethylene glycol-functionalized molecules on PTEG-1. The rest of the molecules in the top layer are omitted for clarity.

Printed by: GVO drukkers & vormgevers B.V.



university of
 groningen

Surface Engineering for Molecular Electronics

PhD thesis

to obtain the degree of PhD at the
 University of Groningen
 on the authority of the
 Rector Magnificus Prof. C. Wijmenga
 and in accordance with
 the decision by the College of Deans.

This thesis will be defended in public on
 Monday 7 December 2020 at 18:00 hours

by

Xinkai Qiu

born on 30 December 1990
 in Guangdong, China

Supervisors

Prof. R. C. Chiechi
Prof. A. Herrmann

Assessment Committee

Prof. G. Palasantzas
Prof. N. Katsonis
Prof. M. Dickey

To my parents

CONTENTS

1 Introduction	1
1.1 Large-area and single-molecule junctions	2
1.2 Molecular monolayers	5
1.2.1 Nonspecific adsorption	6
1.2.2 Langmuir trough-based monolayers	7
1.2.3 Self-assembled monolayers	7
1.3 Fabrication of large-area junctions comprising SAMs	9
1.3.1 Junctions using solid electrodes	9
1.3.2 Junctions using EGaIn electrodes	15
1.4 Charge transport mechanisms	16
1.5 Outline of thesis.	18
References	21
2 Mechanically and Electrically Robust Self-assembled Monolayers for Large-area Tunneling Junctions	35
2.1 Introduction	37
2.2 Results and discussion	38
2.2.1 CP-AFM measurements	39
2.2.2 Mechanical properties	40
2.2.3 Transition voltage spectroscopy	42
2.2.4 DFT calculations.	44
2.2.5 Stability of large-area junctions	46
2.3 Conclusions.	48
2.4 Experimental	49
2.4.1 Preparation of self-assembled monolayers.	49
2.4.2 Characterization of electrical properties	49
2.4.3 PeakForce QNM measurements	50
2.4.4 I/V data processing	51
2.4.5 Estimation of contact area	51
2.4.6 EGaIn stability test	52
References	54
3 Self-regenerating Soft Biophotovoltaic Devices	59
3.1 Introduction	61
3.2 Results and discussion	62
3.2.1 Biophotovoltaic device design	62
3.2.2 Electrode surface area	65
3.2.3 Reticulated cofabricated electrodes	68

3.2.4	Regeneration.	72
3.2.5	SAMs of PSI on fullerene-based linkers	76
3.3	Conclusions.	81
3.4	Experimental	83
3.4.1	Cell growth.	83
3.4.2	Thylakoid membrane preparation	83
3.4.3	Photosystem I purification.	83
3.4.4	Determination of chlorophyll <i>a</i> and protein concentration	84
3.4.5	Fabrication of microfluidic channels.	84
3.4.6	Fabrication of shadow evaporated Au electrode	84
3.4.7	Fabrication of template-stripped Au electrode	84
3.4.8	Fabrication of devices	85
3.4.9	Measurement of photocurrent	85
3.4.10	Measurement of mechanical properties	85
3.4.11	Estimation of surface area of Au ^{SE}	86
3.4.12	Conductance of EGaIn electrodes under strain.	86
3.4.13	Calculation of power conversion efficiency	86
3.4.14	Preparation of PCBA and PSI monolayers	87
3.4.15	AFM	87
3.4.16	EGaIn measurement	88
	References	89
4	Thiol-free Self-assembled Oligoethylene Glycols Enable Robust Air-stable Molecular Electronics	95
4.1	Introduction	97
4.2	Results and discussion	98
4.2.1	Mono- and bilayer characterization	98
4.2.2	Tunneling charge transport measurements	103
4.2.3	Reversible in-place exchange	111
4.2.4	Stability	112
4.3	Conclusions.	116
4.4	Experimental	119
4.4.1	Materials and synthesis	119
4.4.2	Preparation of PTEG-1 monolayer and bilayer	121
4.4.3	Preparation of PTEG-1/alkylGE bilayer	121
4.4.4	Atomic force microscopy (AFM)	121
4.4.5	EGaIn measurements	122
4.4.6	Water Contact Angle	123
4.4.7	Scanning Tunneling Microscopy (STM)	123
4.4.8	X-ray photoelectron spectroscopy (XPS)	123
4.4.9	Ellipsometry	125
4.4.10	Fabrication of soft devices for variable-temperature measurements	127
4.4.11	Variable temperature measurements.	127
4.4.12	X-ray reflectivity	128
4.4.13	Packing density of PTEG-1 SAMs.	130
	References	131

5	<i>In Operando</i> Modulation of Rectification in Molecular Tunneling Junctions Comprising Reconfigurable Molecular Self-assemblies	137
5.1	Introduction	139
5.2	Results and Discussion	140
5.2.1	Characterization of bilayers and monolayers.	140
5.2.2	Charge transport mechanism	144
5.2.3	<i>In operando</i> rectification modulation	147
5.2.4	Stochastic computation	150
5.3	Conclusions.	154
5.4	Experimental	155
5.4.1	Materials and synthesis	155
5.4.2	Preparation of monolayers and bilayers of PTEG-1	159
5.4.3	Preparation of bilayers of PTEG-1/FcTEG	159
5.4.4	EGaIn measurements	159
5.4.5	Fabrication of soft devices for variable-temperature measurements	159
5.4.6	Variable temperature measurements.	160
5.4.7	<i>In operando</i> modulation	161
5.4.8	AFM measurements	162
5.4.9	Water contact angle	162
5.4.10	Ellipsometry	163
5.4.11	Cyclic voltametry, CV	163
5.4.12	Surface tension	163
	References	165
6	Self-assembled Monolayers of Metal Coordination Complexes on Gold Surface	169
6.1	Introduction	171
6.2	Results and discussion	171
6.3	Conclusions.	174
6.4	Experimental	176
6.4.1	Synthesis.	176
6.4.2	Infrared spectroscopy	177
6.4.3	UV-vis spectroscopy	178
6.4.4	Mass spectrometry.	179
6.4.5	Molecular and crystal structures	179
6.4.6	Thermogravimetric analysis	181
6.4.7	Magnetochemical analysis	181
6.4.8	EGaIn measurements	181
6.4.9	Atomic force microscopy.	182
6.4.10	Ellipsometry	183
	References	184
	Summary	187
	Samenvatting	191
	Acknowledgements	195

Curriculum Vitæ	197
List of Publications	199