

University of Groningen

Constructing low-dimensional molecular networks on metal surfaces

Pham, Tuan Anh

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:

2016

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

Citation for published version (APA):

Pham, T. A. (2016). *Constructing low-dimensional molecular networks on metal surfaces*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

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.

Constructing low-dimensional molecular networks on metal surfaces

Tuan Anh Pham

Constructing low-dimensional molecular networks on metal surfaces

Tuan Anh Pham

PhD thesis

University of Groningen

Cover designed by Minh Hoa Lam, Tuan Anh Pham: Artistic representation of the construction of honeycomb molecular networks on metal surfaces.

Print NetzoDruk Groningen bv.

Zernike Institute PhD thesis series 2016-03

ISSN: 1570-1530

ISBN: 978-90-367-8504-4 (printed)

ISBN: 978-90-367-8505-1 (electronic)

The work presented in this thesis was financially supported by the Zernike Institute for Advanced Materials, the Netherlands Organisation for Scientific Research (NWO) and the European research council (ERC).



university of
 groningen

faculty of mathematics and
 natural sciences

zernike institute for
 advanced materials



university of
groningen

Constructing low-dimensional molecular networks on metal surfaces

PhD thesis

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

This thesis will be defended in public on
Friday 22 January 2016 at 16.15 hours

by

Tuấn Anh Phạm

born on 6 June 1984
in Khanh Hoa, Vietnam

Supervisors

Prof.dr. M.A. Stöhr

Prof.dr. P. Rudolf

Assessment committee

Prof.dr. T. Banerjee

Prof.dr. K. Morgenstern

Prof.dr. D. Vanmaekelbergh

TABLE OF CONTENTS

1 Introduction	1
1.1 Motivation	1
1.2 Thesis outline.....	6
References	8
2 Molecules at metal surfaces: An overview	11
2.1 Molecular self-assembly at surfaces.....	12
2.1.1 Basic principles	12
2.1.2 Molecule-molecule interactions	16
2.1.3 Molecule-substrate interactions	20
2.2 On-surface polymerization.....	23
2.2.1 Introduction	23
2.2.2 Ullmann coupling	24
2.2.3 Protecting group chemistry	28
References.....	30
3 Experimental methods	35
3.1 Scanning Tunneling Microscopy (STM).....	36
3.1.1 Introduction	36
3.1.2 Tunneling effect	39
3.2 X-ray photoelectron spectroscopy (XPS)	43
3.3 Low energy electron diffraction (LEED).....	45
References	48
4 Supramolecular self-assembly of metal-free naphthalocyanine on Au(111)	49
4.1 Introduction	50
4.2 Experimental results	51

4.2.1 STM results for H ₂ Nc on Au(111)	51
4.2.2 LEED results for H ₂ Nc on Au(111)	55
4.2.3 XPS results for H ₂ Nc on Au(111)	56
4.3 Conclusions	58
4.4 Experimental methods	58
References	60
5 Self-assembly of pyrene derivatives on Au(111): substituent effects on intermolecular interactions	63
5.1 Introduction	64
5.2 Experimental results	65
5.2.1 Self-assembly of Br ₄ Py on Au(111)	65
5.2.2 Self-assembly of Br ₂ Py on Au(111)	69
5.3 DFT calculations	72
5.4 Conclusions	73
5.5 Experimental methods and computational details	75
5.5.1 Experimental methods	75
5.5.2 Computational details	76
References	78
6 Heat-induced formation of one- or two-coordination molecular networks on Au(111)	81
6.1 Introduction	82
6.2 Experimental results	83
6.2.1 Self-assembly of <i>cis</i> -porphyrins on Au(111)	83
6.2.2 Formation of 1D coordination polymers of <i>cis</i> -porphyrins on Au(111)	88
6.2.3 Self-assembly of <i>trans</i> -porphyrins on Au(111)	95
6.2.4 Formation of 2D coordination networks of <i>trans</i> -porphyrins on Au(111)	97
6.3 Conclusions	98
6.4 Experimental methods and computational details	99
6.4.1 Experimental methods	99
6.4.2 Computational details	99
References	101

7 On-surface polymerization of 1,3,6,8 – tetrabromopyrene on Cu(111) and Au(111)	103
7.1 Introduction	104
7.2 Experimental results	105
7.2.1 On-surface polymerization of Br ₄ Py on Cu(111).....	106
7.2.2 On-surface polymerization of Br ₄ Py on Au(111)	114
7.3 Conclusions	121
7.4 Experimental methods and computational details.....	121
7.4.1 Experimental methods	121
7.4.2 Computational details	122
References	123
8 Protecting group chemistry: A new approach for stepwise on-surface polymerization of biphenyl derivatives on Ag(111)	127
8.1 Introduction	128
8.2 Experimental results	129
8.2.1 STM results on the on-surface polymerization of biphenyl derivatives	129
8.2.2 XPS results on the on-surface polymerization of biphenyl derivatives	135
8.3 Conclusions	138
8.4 Experimental methods and computational details.....	138
8.4.1 Experimental methods	138
8.4.2 Computational details	139
References	140
Summary	143
Samenvatting	147
Author biography	151
List of publications	153
Acknowledgments	155

*To my parents,
my dear wife
and my lovely daughter .*

"Try not to become a man *of success*, but rather
try to become a man of *value*."

- ***Albert Einstein***-