



Universiteit  
Leiden  
The Netherlands

## **Molecular and Nano-engineering with iron, ruthenium and carbon: Hybrid structures for sensing**

Geest, E.P. van

### **Citation**

Geest, E. P. van. (2021, January 14). *Molecular and Nano-engineering with iron, ruthenium and carbon: Hybrid structures for sensing*. Retrieved from <https://hdl.handle.net/1887/139187>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/139187>

**Note:** To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The handle <http://hdl.handle.net/1887/139187> holds various files of this Leiden University dissertation.

**Author:** Geest, E.P. van

**Title:** Molecular and Nano-engineering with iron, ruthenium and carbon: Hybrid structures for sensing

**Issue Date:** 2021-01-14

# **Molecular and Nano-Engineering with Iron, Ruthenium and Carbon: Hybrid Structures for Sensing**

Proefschrift

ter verkrijging van de graad van Doctor aan de Universiteit Leiden,  
op gezag van Rector Magnificus Prof. Mr. C.J.J.M. Stolker,  
volgens besluit van het College voor Promoties

te verdedigen op 14 januari 2021

klokke 10:00

Erik Pieter van Geest

Geboren te Naaldwijk, Nederland

## **Samenstelling Promotiecomissie**

### **Promotores**

Prof. dr. S. Bonnet

Dr. G.F. Schneider

### **Overige leden**

Prof. dr. H.S. Overkleef

Prof. dr. J. Brouwer

Dr. I.M.N. Groot

Prof. dr. J.M. van Ruitenbeek

Dr. G. Molnar (*Laboratoire de Chimie de Coordination, Toulouse, France*)

Prof. dr. H.S.J. van der Zant (*TU Delft*)

The studies described in this thesis were performed at the Leiden Institute of Chemistry at Leiden University, the Netherlands.

ISBN: 978-94-6332-720-6

Printing: GVO Drukkers & Vormgevers

*"Questions are like fire / they need feeding to survive"*

Them Crooked Vultures

*"Man muß die Dinge so einfach wie möglich machen. Aber nicht einfacher."*

Albert Einstein

*To my parents,  
and all who supported me*

## Table of Contents

List of Abbreviations .....	6
1. Introduction .....	9
1.1. Graphene and metal complexes: tools for engineers .....	10
1.2. Engineering with carbon – graphene based sensors.....	11
1.3. Iron complexes as molecular switches: spin crossover .....	18
1.4. Ruthenium complexes – a matter of light and dark.....	26
1.5. Aim of this thesis .....	30
1.6. References .....	31
2. Contactless spin switch sensing by chemo-electric gating of graphene .....	37
2.1. Introduction.....	38
2.1. Results and Discussion .....	40
2.2. Conclusions & Outlook.....	51
2.3. References and Notes .....	52
3. Large-area thin films of the spin crossover complex [Fe(bapbpy)(NCS) <sub>2</sub> ] grown selectively on graphene .....	55
3.1. Introduction.....	56
3.2. Results and Discussion .....	57
3.3. Conclusions & Outlook.....	66
3.4. Acknowledgements.....	67
3.5. References and Notes .....	67
4. Polymer-coated graphene-based gas sensors: chemical fingerprinting by simultaneous sensing.....	69
4.1. Introduction.....	70
4.2. Results and Discussion .....	72
4.3. Chemical fingerprint (CF) vapor sensors .....	80
4.4. Conclusions & Outlook.....	87
4.5. References and Notes .....	88
5. Monitoring a ruthenium-based photoreaction with graphene on paper ....	89
5.1. Introduction.....	90
5.2. Results and Discussion .....	92

5.3.	Conclusions & Outlook.....	100
5.4.	Acknowledgements.....	101
5.5.	References and Notes.....	101
6.	Reducing the translocation speed of DNA in solid-state nanopores by photo-labile ruthenium complex decoration .....	103
6.1.	Introduction.....	104
6.2.	Results and Discussion .....	105
6.3.	Conclusions & Outlook.....	111
6.4.	Acknowledgements.....	111
6.5.	References and Notes.....	111
7.	[Ru(3)(biq)(STF-31)] <sup>2+</sup> : A lock-and-kill anticancer PACT agent .....	113
7.1.	Introduction.....	114
7.2.	Results and Discussion .....	116
7.3.	Conclusions & Outlook.....	122
7.4.	References and Notes.....	123
8.	Summary, Conclusions & Outlook .....	125
8.1	Summary.....	126
8.2	Conclusions and Outlook .....	133
	Appendix Chapter 2 .....	137
	Appendix Chapter 3 .....	153
	Appendix Chapter 4 .....	165
	Appendix Chapter 5 .....	185
	Appendix Chapter 6 .....	191
	Appendix Chapter 7 .....	195
	Samenvatting, conclusies en vooruitzichten .....	209
	List of publications.....	223
	Curriculum Vitae .....	225
	Acknowledgements .....	227

## List of Abbreviations

( $\mu$ )RNA	(micro)-ribonucleic acid
(ADF)-STEM	(annular dark-field)- scanning transmission electron microscopy
(ATR)-IR	(attenuated total reflection) infrared spectroscopy
(ct)DNA	(calf thymus) deoxyribonucleic acid
(LC/HR)-MS	(liquid chromatography/high resolution) mass spectrometry
(r)GO	(reduced) graphene oxide
acac	acetylacetonate
AFM	atomic force microscopy
ANO-RCC	atomic natural orbitals (relativistic and (semi-)core correlation)
APS	ammonium persulfate
APTES	3-aminopropyltriethoxysilane
babppy	N,N'-di(pyrid-2-yl)-2,2'-bipyridine-6,6'-diamine
bbpya	N,N-bis(2-2'-bipyrid-6-yl)amine
biq	2,2'-biquinoline
bpy	2,2'-bipyridine
bpz	dihydrobis(pyrazolyl)borate
CAB	cellulose acetate butyrate
CAS(SCF)	complete active space (self-consistent field)
CEG	chemo-electric gating
CF	chemical fingerprint
CITS	current-imaging-tunneling spectroscopy
dAMP	2-deoxyadenosine monophosphate
dCMP	2-deoxycytidine monophosphate
dGMP	2-deoxyguanosine monophosphate
dTMP	2-deoxythymidine monophosphate
DCC	N,N'-dicyclohexylcarbodiimide
DCM	dichloromethane
DEME-TFSI	diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dppz	dipyrido[3,2-a:2',3'-c]phenazine
EDTA	ethylenediaminetetraacetic acid



EDX	energy-dispersive X-ray spectroscopy
Elem. Anal.	elemental analysis
EM	emission wavelength
Et <sub>2</sub> O	diethyl ether
EX	excitation wavelength
GC	gas chromatography
GFET	graphene field effect transistor
GLUT1	glucose transporter, type 1
GS	ground state
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
HOPG	highly oriented pyrolytic graphite
HS	high spin
Htrz	1H-1,2,4-triazole
IC <sub>50</sub>	half maximal inhibitory concentration
ICYTES	3-isocyanatepropyltriethoxysilane
IL	ionic liquid
IP	intermediate phase
IPA	isopropyl alcohol
ITO	indium tin oxide
KNN	k-nearest neighbor
LDA	local density approximation
LED	light-emitting diode
LF	ligand field
LS	low spin
MC	metal center
MEAS	measurement (transistor name)
MeOH	methanol
MOF	metal organic framework
MLCT	Metal-to-ligand charge transfer
NAMPT	nicotinamide phosphoribosyltransferase
NB	Naive Bayesian
NH <sub>2</sub> trz	4-amino-1,2,4-triazole
NMR	nuclear magnetic resonance
NP	nanoparticle
OTMS	octadecyltrimethoxysilane
PACT	photoactivated chemotherapy
PAH	polyaromatic hydrocarbon
PCA	principle component analysis
PDMS	polydimethylsiloxane

PDT	photodynamic therapy
phen	1,10-phenanthroline
pic	2-pyridine carboxylate
PMMA	poly(methyl methacrylate)
PTFE	polytetrafluoroethylene
QY	quantum yield
RBF	radial basis function
REF	reference (transistor name)
RF	Random Forest
ROS	reactive oxygen species
RPA	random phase approximation
RT	room temperature
sal	saliva
SCO	spin crossover
SERS	surface-enhanced Raman spectroscopy
SiN	silicon nitride
SMV	Support Vector Machines
SPPR	surface plasmon-polariton resonance
SPR	surface plasmon resonance
SQUID	superconducting quantum interference device
STF-31	4-((4-t-butyl)phenylsulfonamido)methyl)-N-(pyridin-3-yl)benzamide
STM	scanning tunneling microscopy
TCYTES	3-thiocyanatepropyltriethoxysilane
TEM	transmission electron microscopy
TLC	thin-layer chromatography
tpy	2,2':6',2''-terpyridine
UV-vis	ultraviolet-visible spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction