

University of Groningen

Hydrogelators

Canrinus, Tjalling Rienk

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:

2019

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

Citation for published version (APA):

Canrinus, T. R. (2019). *Hydrogelators: mechanisms, applications, and rational design*. [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.

Hydrogelators

Mechanisms, applications, and rational design

Tjalling Rienk Canrinus

The work described in this thesis was carried out at Stratingh Institute for Chemistry, University of Groningen (The Netherlands)



university of
 groningen

faculty of science
 and engineering

stratingh institute
 for chemistry

This work was financially supported by Ministry of Education, Culture and Science (Gravitation program 024.001.035)



Research Center for
 Functional Molecular Systems

Gravitation Program - The Netherlands

Printed by Ipskamp Printing, Enschede, The Netherlands

Cover picture: Dark field photographs of gels in 4 mL glass vials.

ISBN: (Print) 978-94-034-1742-4

ISBN: (Ebook) 978-94-034-1741-7



university of
groningen

Hydrogelators

Mechanisms, applications, and rational design

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 21 June 2019 at 16:15 hours

by

Tjalling Rienk Canrinus

born on 21 February 1990
in Leeuwarden, the Netherlands

Supervisors

Prof. W.R. Browne

Prof. B.L. Feringa

Assessment Committee

Prof. S. Otto

Prof. R.J.M. Nolte

Prof. M. Tromp

Table of Content

Chapter 1

An introduction to hydrogels	9
Introduction	11
Cyclohexane based hydrogelators	12
Three fold symmetric gelators based on the benzene tricarboxylic acid core	18
Linear hydrogelators based on amino acids	18
Challenges and Chapters	22
Bibliography	23

Chapter 2

Remarkable solvent isotope	27
dependence on gelation strength in low molecular weight hydrogelators	27
Abstract	27
Introduction	29
Supporting Information	34
Bibliography	34
Supporting figures	37

Chapter 3

Label free spectroscopic determination of formation of and molecular packing in cyclohexane based hydrogelator fibres	41
Abstract	41
Introduction	43
Results	44
Dark field microscopy	46
Cryo-TEM of CH-Leu and CH-Abu at time interval	46
Time profile of SAXS of CH-Leu	48
Crystal structure and its relation to gel fibres for CH-Abu	51
Raman of CH-Tyr and CH-Abu crystals and CH-Abu fibres	51
Discussion	52
Conclusion	53
Acknowledgments	53
Bibliography	53

Chapter 4

Tyrosine based cyclohexane triamide hydrogelators	57
Abstract	57
Introduction	59
Results	61
Synthesis	61
Spectroscopic properties	61
Analysis of single crystals:	61
Polarized Raman	63
Analysis of mixtures of gelators	64

Conclusion and Outlook	65
Bibliography	65

Chapter 5

Supramolecular Low Molecular Weight Hydrogelator Stabilization of SERS Active Aggregated Nanoparticles for Solution and Gas Sensing	69
Abstract	69
Introduction	71
Results and Discussion	72
Distribution of aggregated colloid in hydrogel matrices	73
Detection of gases by hydrogel stabilized colloids through reversible gas uptake and release.	74
Long term stability of SERS scaffolds	74
SERS activity before and after reconstitution of lyophilized gels.	75
Conclusion	77
Supporting information	78
Acknowledgements	78
Bibliography	78
Supporting Figures	80

Chapter 6

Benzene triamide amino acid hydrogelators	89
Abstract	89
Introduction	91
Synthesis	91
Gel Properties	92
Polarised Raman microspectroscopy	93
Conclusion	94
Bibliography	94

Appendix A

Materials and Instrumentation	97
General remarks.	97
Gelation by heating and cooling cycle.	97
Gelation by pH jumping.	97
Gelation of with Au or Ag nanoparticles.	97
NMR	97
FTIR	97
UV-Vis	97
Circular Dichroism	97
Fluorescence	98
Raman	98
Dropping Ball	98
Rheology	98
Transmission Electron Microscopy	98
Cryogenic Transmission Electron Microscopy	98
Single Crystal X-ray	99
Dark field microscope	99

Small Angle X-ray Scattering	99
Polarized Raman	99

Appendix B

Synthesis and Characterisation	103
CH-Gly	103
CH-Ala	103
CH-Val	103
CH-Leu	104
CH-Ile	104
CH-Met	104
CH-Phe	104
CH-Trp	104
CH-Abu	105
CH-Nva	105
CH-Nle	105
CH-Tyr	105
Elemental Analysis	106
BTA-Val	106
BTA-Met	106
Preparation of Gold colloid	106
Preparation of Silver colloid:	106
Bibliography	107

Appendix C

Structures of compounds	109
--------------------------------	-----

Appendix D

Summary	111
----------------	-----

Appendix E

Samenvatting	115
---------------------	-----

Appendix F

Acknowledgments	119
------------------------	-----

1