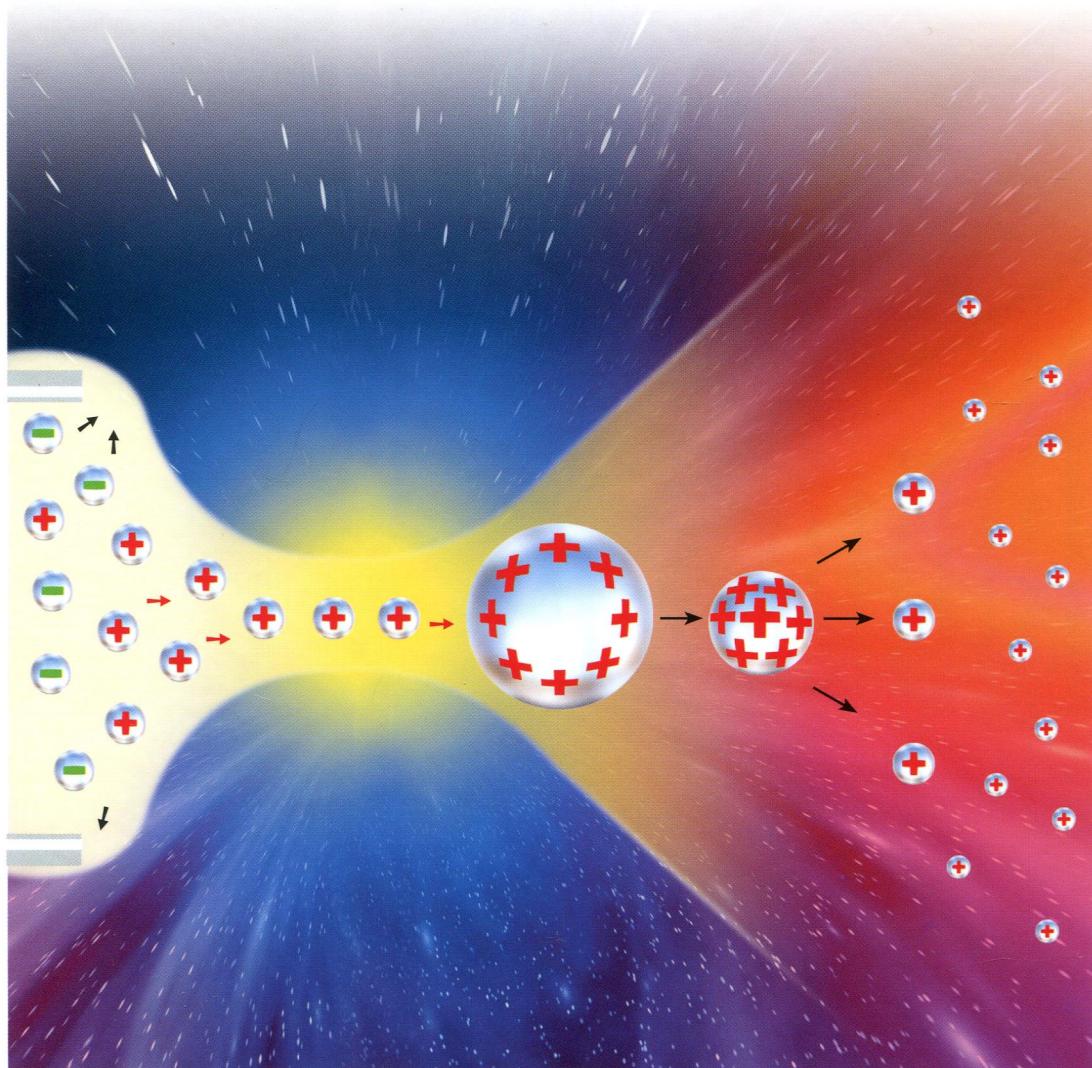


Edited by Christoph A. Schalley

WILEY-VCH

Analytical Methods in Supramolecular Chemistry

Second, Completely Revised and Enlarged Edition
Volume 1



The Editor**Prof. Dr. Christoph Schalley**

Freie Universität Berlin
Institut für Chemie und Biochemie
Takustr. 3
14195 Berlin
Germany

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication**Data**

A catalogue record for this book is available from the British Library.

**Bibliographic information published by the
Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2012 Wiley-VCH Verlag & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Laserwords Private Ltd.,
Chennai

Printing and Binding betz-druck GmbH,
Darmstadt

Cover Design Adam Design, Weinheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

Print ISBN: 978-3-527-32982-3

ePDF ISBN: 978-3-527-64415-5

eBook ISBN: 978-3-527-64413-1

ePub ISBN: 978-3-527-64414-8

Mobi ISBN: 978-3-527-64416-2

Contents to Volume 1

Preface XIII

List of Contributors XV

1	Introduction	1
	<i>Lena Kaufmann and Christoph A. Schalley</i>	
1.1	Some Historical Remarks on Supramolecular Chemistry	1
1.2	The Noncovalent Bond: a Brief Overview	2
1.3	Basic Concepts in Supramolecular Chemistry	4
1.3.1	Molecular Recognition: Molecular Complementarity	5
1.3.2	Chelate Effects and Preorganization: Entropy Factors	5
1.3.3	Cooperativity and Multivalency	7
1.3.4	The Three “Selves”: Self-Assembly, Self-Organization, Self-Sorting	8
1.3.5	Template Effects	12
1.3.6	Self-Replication and Supramolecular Catalysis	13
1.3.7	Molecular Devices and Machines: Implementing Function	15
1.3.8	Extended Assemblies: Liquid Crystals and Supramolecular Gels	18
1.4	Conclusions: Diverse Methods for a Diverse Research Area	21
	References	22
2	Quantitative Analysis of Binding Properties	27
	<i>Keiji Hirose</i>	
2.1	Theoretical Principles	27
2.1.1	The Binding Constants and Binding Energies	27
2.1.2	A General View on the Determination of Binding Constants	28
2.1.3	Guideline for Experiments	29
2.2	A Practical Course of Binding Constant Determination by UV/Vis Spectroscopy	29
2.2.1	Determination of Stoichiometry	29
2.2.2	Evaluation of Complex Concentration	33
2.2.3	Precautions to Be Taken When Setting Concentration Conditions for the Titration Experiment	34
2.2.3.1	Correlation between $[H]_0$, $[G]_0$, x , and K	34
2.2.3.2	How to Set $[H]_0$	36

2.2.3.3	How to Set $[G]_0$	36
2.2.4	Data Treatment	41
2.2.4.1	General View	41
2.2.4.2	Rose–Drago Method for UV/Vis Spectroscopy	41
2.2.4.3	Estimation of Error	43
2.2.5	Conclusion for UV/Vis Spectroscopic Method	43
2.3	Practical Course of Action for NMR Spectroscopic Binding Constant Determination	44
2.3.1	Determination of Stoichiometry	45
2.3.2	Evaluation of Complex Concentration	47
2.3.3	Data Treatment for NMR Method	47
2.3.3.1	Rose–Drago Method for NMR Spectroscopy	47
2.3.3.2	Estimation of Error for NMR Method	49
2.3.3.3	Nonlinear Least Square Data Treatment of NMR Titration Method	49
2.3.3.4	Estimation of Error for Nonlinear Least Square Method of NMR Spectroscopy	52
2.4	Other Important Examples with Practical Actions of Data Treatment	53
2.4.1	Exemplified Data Treatment for a Fluorescence Quench System	53
2.4.1.1	Static Quenching Model of a 1 : 1 Complexation System	53
2.4.1.2	Estimation of Error for Approximated Straight-Line Parameters by Linear Regression	54
2.4.2	Exemplified Data Treatment for a 1 : 2 Complexation System	55
2.4.2.1	Typical Case Study for a 1 : 2 Complexation System	55
2.4.2.2	Estimation of Error for General Functions	57
2.4.2.3	Modification for 1 : 2 Complexations with Guest Probe Proton Monitoring	57
2.4.3	Modification for 2 : 1 Complexations	57
2.4.4	Data Treatment for a System Having 1 : 1 and 2 : 1 Complexations	58
2.5	Conclusion	59
	References	66
3	Isothermal Titration Calorimetry in Supramolecular Chemistry	67
	<i>Franz P. Schmidtchen</i>	
3.1	Introduction	67
3.2	The Thermodynamic Platform	69
3.3	Acquiring Experimental Calorimetric Data	72
3.3.1	Data Evaluation	81
3.4	Extending the Measurement Range	88
3.4.1	Expanding the Scope of ITC	93
3.5	Perspectives	100
	Acknowledgment	100
	References	101

4	Extraction Methods	105
	<i>Holger Stephan, Manja Kubeil, Kerstin Gloe, and Karsten Gloe</i>	
4.1	Introduction	105
4.2	The Extraction Technique	106
4.3	The Technical Process	108
4.4	The Extraction Equilibrium	109
4.5	Principles of Supramolecular Extraction	112
4.6	Examples of Supramolecular Extraction	114
4.7	Conclusions and Future Perspectives	124
	Acknowledgments	125
	References	125
5	Mass Spectrometry and Gas Phase Chemistry of Supramolecules	129
	<i>Dominik P. Weimann, Michael Kogej, and Christoph A. Schalley</i>	
5.1	Introduction	129
5.2	Instrumentation	130
5.2.1	Ionization Techniques Suitable for Noncovalent Species	131
5.2.1.1	Matrix-Assisted Laser Desorption/Ionization	131
5.2.1.2	Electrospray Ionization	133
5.2.1.3	Resonance-Enhanced Multiphoton Ionization (REMPI)	134
5.2.1.4	Ionization of Noncovalent Species	135
5.2.2	Mass Analyzers	135
5.2.2.1	Quadrupole Instruments and Quadrupole Ion Traps	137
5.2.2.2	Time-of-Flight	138
5.2.2.3	Ion Cyclotron Resonance	139
5.3	Particularities and Limitations of Mass Spectrometry	141
5.4	Beyond Analytical Characterization: Tandem MS Experiments for the Examination of the Gas-Phase Chemistry of Supramolecules	143
5.4.1	Collision-Induced Decay	144
5.4.2	Infrared-Multiphoton Dissociation	145
5.4.3	Blackbody Infrared Radiative Dissociation	146
5.4.4	Electron-Capture Dissociation and Electron Transfer Dissociation	146
5.4.5	Bimolecular Reactions: H/D-Exchange and Gas-Phase Equilibria	147
5.5	Selected Examples	147
5.5.1	Analytical Characterization: Exact Mass, Isotope Patterns, Charge State, Stoichiometry, Impurities	148
5.5.2	Structural Characterization of Supramolecules	150
5.5.2.1	The Mechanical Bond: How to Distinguish Molecules with Respect to Their Topology	150
5.5.2.2	Encapsulation of Guest Molecules in Self-Assembling Capsules	151
5.5.3	Ion Mobility: a Zwitterionic Serine Octamer?	159
5.5.4	Mass Spectrometry for the Detection of Chirality	162
5.5.5	Reactivity Studies of Supramolecules in Solution	164
5.5.5.1	Ligand Exchange in Dimeric Helicates	165

5.5.5.2	The Double-Syringe Technique for Monitoring Fast Complex-Formation Kinetics in Solution	169
5.5.6	Reactivity in the Gas Phase: Isolated Species Instead of Dynamic Exchange Processes	173
5.5.6.1	Metallosupramolecular Squares and Cages: a Supramolecular Equivalent to Neighbor Group Assistance	173
5.5.6.2	A Surprising Dendritic Effect: Switching Fragmentation Mechanisms	178
5.5.6.3	Gas-Phase H/D Exchange for Analyzing Molecular Mobility	182
5.5.7	Determining Thermochemical Data: the Influence of the Environment	188
5.5.7.1	Crown Ether-Alkali Complexes: Questioning the Best-Fit Model	188
5.5.7.2	BIRD: Arrhenius Kinetics of Oligonucleotide Strand Separation in the Gas Phase	190
5.6	Conclusions	191
	References	192
6	Diffusion NMR in Supramolecular Chemistry and Complexed Systems	197
	<i>Yoram Cohen, Liat Avram, Tamar Evan-Salem, Sarit Slovak, Noam Shemesh, and Limor Frish</i>	
6.1	Introduction	197
6.2	Concepts of Molecular Diffusion	198
6.3	Measuring Diffusion with NMR	198
6.3.1	The Basic Pulse Sequence	198
6.3.2	The Stimulated Echo (STE) Diffusion Sequence	201
6.3.3	Technical Issues in Diffusion NMR	203
6.3.4	The LED and BPLED Sequences	205
6.3.5	DOSY – Diffusion Ordered Spectroscopy	206
6.4	Applications of Diffusion NMR in Supramolecular Chemistry: Selected Examples	209
6.4.1	Binding and Association Constants	209
6.4.2	Encapsulation and Molecular Capsules	216
6.4.3	Molecular Size, Shape, and Self-Aggregation	225
6.4.4	Diffusion as a Filter: Virtual Separation and Ligand Screening	245
6.4.5	Organometallics, Reactive Intermediates, and Supercharged Supramolecular Systems	250
6.4.6	Supramolecular Polymers	254
6.5	Advantages and Limitations of High Resolution Diffusion NMR	259
6.6	Diffusion NMR and Chemical Exchange	260
6.7	Diffusion Modes and Signal Decay in Diffusion MR Experiments	265
6.8	Applications of Diffusion NMR in Complex Systems	269
6.8.1	Zeolites and Carbon Nanotubes	269
6.8.2	Micelles and Emulsions	272

6.8.3	Liposomes	274
6.8.4	Organic Conductors	274
6.8.5	Biological Systems: Cells and Tissues	275
6.9	Summary and Outlook	276
	References	279
7	Photophysics and Photochemistry of Supramolecular Systems	287
	<i>Bernard Valeur, Mário Nuno Berberan-Santos, Monique M. Martin, and Pascal Plaza</i>	
7.1	Introduction	287
7.2	Spectrophotometry and Spectrofluorometry	288
7.2.1	Determination of the Stoichiometry and Association Constants of Supramolecular Complexes from Spectrophotometric or Spectrofluorometric Titrations	288
7.2.2	Cooperativity and Anticooperativity	290
7.2.3	Possible Differences in Binding Constants in the Ground State and in the Excited State	293
7.2.4	Information on Photoinduced Processes from Fluorescence Spectra	293
7.2.4.1	Photoinduced Electron Transfer in a Calixarene-Based Supermolecule Designed for Mercury Ion Sensing	293
7.2.4.2	Excitation Energy Transfer in an Inclusion Complex of a Multichromophoric Cyclodextrin with a Fluorophore	295
7.3	Time-Resolved Fluorescence Techniques	296
7.3.1	General Principles	297
7.3.2	Pulse Fluorometry	300
7.3.3	Phase-Modulation Fluorometry	302
7.3.3.1	Phase Fluorometers Using a Continuous Light Source and an Electro-Optic Modulator	302
7.3.3.2	Phase Fluorometers Using the Harmonic Content of a Pulsed Laser	304
7.3.4	Data Analysis	304
7.3.5	Lifetime Standards	306
7.3.6	Examples of Application	306
7.3.6.1	Photoinduced Electron Transfer in a Self-Assembled Zinc Naphthalocyanine–Fullerene Diad	306
7.3.6.2	Excitation Energy Transfer in a Self-Assembled Zinc Porphyrin–Free Base Porphyrin Diad	307
7.3.6.3	Excimer Formation of Cyanobiphenyls in a Calix[4]resorecinarene Derivative	309
7.3.6.4	Recovery of the Distributions of Decay Times from the Fluorescence Decays in Supramolecular Multichromophoric Systems	309
7.4	Fluorescence Anisotropy	311
7.4.1	General Principles	312
7.4.2	Examples of Application	316

7.4.2.1	Supramolecular Polymer Length	316
7.4.2.2	Excitation Energy Hopping in Multichromophoric Cyclodextrins	316
7.5	Transient Absorption Spectroscopy	319
7.5.1	General Principles	320
7.5.2	Pump–Probe Spectroscopy with Ultrashort Laser Excitation	321
7.5.2.1	White Light Continuum Generation	321
7.5.2.2	Broadband Femtosecond Pump–Probe Set-up	323
7.5.2.3	Time-Resolved Differential Absorption Measurements	325
7.5.2.4	Data Analysis	326
7.5.3	Examples of Application	328
7.5.3.1	Charge Separation in Porphyrin–Fullerene Diads	328
7.5.3.2	Cation Photorelease from a Crown-Ether Complex	329
7.5.3.3	Light-Driven Cationic Shuttle	330
7.6	Concluding Remarks	332
	References	334
8	Circular Dichroism Spectroscopy	337
	<i>Marie Urbanová and Petr Maloň</i>	
8.1	Basic Considerations	337
8.1.1	Circular Dichroism	337
8.1.2	Variants of Chiroptical Methods	340
8.1.3	Advantages and Limits of Circular Dichroism Spectroscopies	341
8.1.3.1	Chiral and Parent Non-chiral Spectroscopies	341
8.1.3.2	Electronic and Vibrational Circular Dichroism	341
8.1.3.3	Instrumentation	343
8.1.3.4	Calculations	343
8.2	Measurement Techniques (Methodology of CD Measurement)	343
8.2.1	Electronic Circular Dichroism Measurements	347
8.2.2	Vibrational Circular Dichroism Measurements	347
8.3	Processing of Circular Dichroism Spectra	350
8.3.1	Intensity Calibration in VCD Spectroscopy	351
8.3.2	Baseline Corrections and Reliability in VCD	352
8.3.3	Advanced Processing of Circular Dichroism Spectra	354
8.4	Theory	356
8.4.1	Rotational Strength	356
8.4.2	Mechanisms Generating Optical Activity	356
8.4.3	<i>Ab initio</i> Calculations	358
8.5	Examples of Vibrational Circular Dichroism Applications	359
8.5.1	Absolute Configuration and Detailed Structural Parameters	359
8.5.2	Solution Structure of Biomolecules	361
8.5.3	Supramolecular Systems	362
8.6	Concluding Remarks	363
	Abbreviations	364
	References	364

Contents to Volume 2

Preface XIII

List of Contributors XV

- 9 **Electrochemical Methods** 371
Paola Ceroni, Alberto Credi, and Margherita Venturi
- 10 **Crystallography and Crystal Engineering** 459
Kari Rissanen
- 11 **Scanning Probe Microscopy** 499
Bianca A. Hermann and Regina Hoffmann-Vogel
- 12 **Single-Molecule Force Spectroscopy of Supramolecular Complexes** 559
Tobias Schroeder, Volker Walhorn, Jochen Mattay, and Dario Anselmetti
- 13 **Confocal Laser Scanning Microscopy: a Versatile Spectroscopic Tool for the Investigation of Molecular Gels** 607
Anthony D'Aléo, André Del Guerzo, and Frédéric Fages
- 14 **Transmission Electron Microscopy (TEM) of Radiation Sensitive Supramolecular Architectures –Strategies for a Comprehensive Structure Characterization** 629
Christoph Böttcher
- 15 **The Characterization of Synthetic Ion Channels and Pores** 711
Stefan Matile and Naomi Sakai
- 16 **Theoretical Methods for Supramolecular Chemistry** 743
Barbara Kirchner and Markus Reiher
- Index 795