

Contents

Preface XIII

List of Contributors XV

1	Introduction	1
	<i>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	Self-assembly and Self-organization	8
1.3.5	Template Effects	10
1.3.6	Self-replication and Supramolecular Catalysis	11
1.3.7	Molecular Devices and Machines: Implementing Function	13
1.4	Conclusions: Diverse Methods for a Diverse Research Area	14
	References and Notes	15
2	Determination of Binding Constants	17
	<i>Keiji Hirose</i>	
2.1	Theoretical Principles	17
2.1.1	The Binding Constants and Binding Energies	17
2.1.2	A General View on the Determination of Binding Constants	18
2.1.3	Guideline for Experiments	19
2.2	A Practical Course of Binding Constant Determination by UV/vis Spectroscopy	19
2.2.1	Determination of Stoichiometry	19
2.2.2	Evaluation of Complex Concentration	23
2.2.3	Precautions to be Taken when Setting Up Concentration Conditions of the Titration Experiment	25
2.2.3.1	Correlation between $[H]_0$, $[G]_0$, x and K	25
2.2.3.2	How to Set Up $[H]_0$	27

2.2.3.3	How to Set Up $[G]_0$	27
2.2.4	Data Treatment	32
2.2.4.1	General View	32
2.2.4.2	Rose–Drago Method for UV/vis Spectroscopy	33
2.2.4.3	Estimation of Error	35
2.2.5	Conclusion for UV/vis Spectroscopic Method	35
2.3	Practical Course of Action for NMR Spectroscopic Binding Constant Determination	36
2.3.1	Determination of Stoichiometry	37
2.3.2	Evaluation of Complex Concentration	39
2.3.3	Data Treatment for NMR Method	39
2.3.3.1	Rose–Drago Method for NMR Spectroscopy	39
2.3.3.2	Estimation of Error for NMR Method	40
2.3.3.3	Nonlinear Least Square Data Treatment of NMR Titration Method	40
2.3.3.4	Estimation of Error for Nonlinear Least Square Method of NMR Spectroscopy	44
2.4	Conclusion	45
	References and Notes	54
3	Isothermal Titration Calorimetry in Supramolecular Chemistry	55
	<i>Franz P. Schmidtchen</i>	
3.1	Introduction	55
3.2	The Thermodynamic Platform	56
3.3	Acquiring Calorimetric Data	60
3.4	Extending the Applicability	70
3.5	Perspectives	75
	Acknowledgement	76
	References	77
4	Extraction Methods	79
	<i>Holger Stephan, Stefanie Juran, Bianca Antonioli, Kerstin Gloe and Karsten Gloe</i>	
4.1	Introduction	79
4.2	The Extraction Technique	80
4.3	The Technical Process	83
4.4	The Extraction Equilibrium	84
4.5	Principles of Supramolecular Extraction	87
4.6	Examples of Supramolecular Extraction	89
4.7	Conclusions and Future Perspectives	100
	Acknowledgements	100
	References	101
5	Mass Spectrometry and Gas Phase Chemistry of Supramolecules	104
	<i>Michael Kogej and Christoph A. Schalley</i>	
5.1	Introduction	104
5.2	Instrumentation	105
5.2.1	Ionization Techniques Suitable for Noncovalent Species	106

5.2.1.1	Matrix-assisted Laser Desorption/Ionization (MALDI)	106
5.2.1.2	Electrospray Ionization (ESI)	108
5.2.1.3	Resonance-enhanced Multiphoton Ionization (REMPI)	110
5.2.1.4	Ionization of Noncovalent Species	110
5.2.2	Mass Analyzers	111
5.2.2.1	Quadrupole Instruments and Quadrupole Ion Traps	111
5.2.2.2	Time-of-flight (TOF)	113
5.2.2.3	Ion Cyclotron Resonance (ICR)	115
5.3	Particularities and Limitations of Mass Spectrometry	117
5.4	Beyond Analytical Characterization: Tandem MS Experiments for the Examination of the Gas-phase Chemistry of Supramolecules	119
5.4.1	Collision-induced Decay (CID)	120
5.4.2	Infrared-multiphoton Dissociation (IRMPD)	120
5.4.3	Blackbody Infrared Dissociation (BIRD)	121
5.4.4	Electron-capture Dissociation (ECD) and Electron Transfer Dissociation (ETD)	122
5.4.5	Bimolecular Reactions: H/D-exchange and Gas-phase Equilibria	122
5.5	Selected Examples	123
5.5.1	Analytical Characterization: Exact Mass, Isotope Patterns, Charge State, Stoichiometry, Impurities	125
5.5.2	Structural Characterization of Supramolecules	126
5.5.2.1	The Mechanical Bond: How to Distinguish Molecules with Respect to Their Topology	126
5.5.2.2	Encapsulation of Guest Molecules in Self-assembling Capsules	127
5.5.3	Ion Mobility: A Zwitterionic Serine Octamer?	138
5.5.4	Mass Spectrometry for the Detection of Chirality	140
5.5.5	Reactivity Studies of Supramolecules in Solution	142
5.5.6	Reactivity in the Gas Phase: Isolated Species instead of Dynamic Interconverting Complexes	147
5.5.6.1	Metallosupramolecular Squares: A Supramolecular Equivalent to Neighbor Group Assistance	147
5.5.6.2	A Surprising Dendritic Effect: Switching Fragmentation Mechanisms	151
5.5.7	Determining Thermochemical Data: The Influence of the Environment	154
5.5.7.1	Crown Ether – Alkali Complexes: Questioning the Best-fit Model	154
5.5.7.2	BIRD: Arrhenius Kinetics of Oligonucleotide Strand Separation in the Gas Phase	157
5.6	Conclusions	157
	References and Notes	159
6	Diffusion NMR in Supramolecular Chemistry	163
	<i>Yoram Cohen, Liat Avram, Tamar Evan-Salem and Limor Frish</i>	
6.1	Introduction	163
6.2	Concepts of Molecular Diffusion	164
6.3	Measuring Diffusion with NMR	164

6.3.1	The Basic Pulse Sequence	164
6.3.2	The Stimulated Echo (STE) Diffusion Sequence	168
6.3.3	Technical Issues in Diffusion NMR	169
6.3.4	The LED and BPLED Sequences	171
6.3.5	DOSY – Diffusion Ordered Spectroscopy	173
6.4	Applications of Diffusion NMR in Supramolecular Chemistry: Selected Examples	175
6.4.1	Binding and Association Constants	175
6.4.2	Encapsulation and Molecular Capsules	181
6.4.3	Molecular Size, Shape and Self-aggregation	193
6.4.4	Diffusion as a Filter: Virtual Separation and Ligand Screening	203
6.4.5	From Organometallics to Supercharged Supramolecular Systems	207
6.5	Advantages and Limitations of Diffusion NMR	209
6.6	Diffusion NMR and Chemical Exchange	210
6.7	Summary and Outlook	215
	References and Notes	216
7	Photophysics and Photochemistry of Supramolecular Systems	220
	<i>Bernard Valeur, Mário Nuno Berberan-Santos and Monique M. Martin</i>	
7.1	Introduction	220
7.2	Spectrophotometry and Spectrofluorometry	221
7.2.1	Determination of the Stoichiometry and Association Constant of Supramolecular Complexes from Spectrophotometric or Spectrofluorometric Titrations	221
7.2.2	Cooperativity and Anticooperativity	224
7.2.3	Possible Differences in Binding Constants in the Ground State and in the Excited State	226
7.2.4	Information on Photoinduced Processes from Fluorescence Spectra	227
7.2.4.1	Photoinduced Electron Transfer in a Calixarene-based Supermolecule Designed for Mercury Ion Sensing [10]	227
7.2.4.2	Excitation Energy Transfer in an Inclusion Complex of a Multichromophoric Cyclodextrin with a Fluorophore	229
7.3	Time-resolved Fluorescence Techniques	230
7.3.1	General Principles	231
7.3.2	Pulse Fluorometry	233
7.3.3	Phase-modulation Fluorometry	235
7.3.3.1	Phase Fluorometers using a Continuous Light Source and an Electro-optic Modulator	235
7.3.3.2	Phase Fluorometers using the Harmonic Content of a Pulsed Laser	237
7.3.4	Data Analysis	237
7.3.5	Examples	238
7.3.5.1	Photoinduced Electron Transfer in a Self-assembled Zinc Naphthalocyanine–Fullerene Diad	238

7.3.5.2	Excitation Energy Transfer in a Self-assembled Zinc Porphyrin–Free Base Porphyrin Diad	240
7.3.5.3	Excitation Energy Transfer in an Inclusion Complex of a Multichromophoric Cyclodextrin with a Fluorophore	241
7.3.5.4	Excimer Formation of Cyanobiphenyls in a Calix[4]resorcinarene Derivative	241
7.4	Fluorescence Anisotropy	243
7.4.1	Principles	244
7.4.2	Examples	249
7.4.2.1	Supramolecular Polymer Length	249
7.4.2.2	Excitation Energy Hopping in Multichromophoric Cyclodextrins	251
7.5	Transient Absorption Spectroscopy	253
7.5.1	General Principles	253
7.5.2	Pump-probe Spectroscopy with Subpicosecond Laser Excitation	254
7.5.2.1	White Light Continuum Generation	254
7.5.2.2	Subpicosecond Pump-continuum Probe Set-up	255
7.5.2.3	Time-resolved Differential Absorption Measurements	257
7.5.2.4	Data Analysis	257
7.5.3	Examples of Application	258
7.5.3.1	Charge Separation in Porphyrin–Fullerene Diads	258
7.5.3.2	Cation Photorelease from a Crown-ether Complex	260
7.6	Concluding Remarks	262
	References and Notes	262
8	Circular Dichroism Spectroscopy	265
	<i>Marie Urbanová and Petr Maloň</i>	
8.1	Basic Considerations	265
8.1.1	Circular Dichroism	265
8.1.2	Variants of Chiroptical Methods	268
8.1.3	Advantages and Limits of Circular Dichroism Spectroscopies	269
8.1.3.1	Chiral and Parent Non-chiral Spectroscopies	269
8.1.3.2	Electronic and Vibrational Circular Dichroism	269
8.1.3.3	Instrumentation	270
8.1.3.4	Calculations	270
8.2	Measurement Techniques (Methodology of CD Measurement)	270
8.2.1	Electronic Circular Dichroism Measurements	272
8.2.2	Vibrational Circular Dichroism Measurements	272
8.3	Processing of Circular Dichroism Spectra	275
8.3.1	Intensity Calibration in VCD Spectroscopy	276
8.3.2	Baseline Corrections and Reliability in VCD	277
8.3.3	Advanced Processing of Circular Dichroism Spectra	277
8.4	Theory	279
8.4.1	Rotational Strength	279
8.4.2	Mechanisms Generating Optical Activity	280
8.4.3	<i>Ab initio</i> Calculations	282

8.5	Examples of Vibrational Circular Dichroism Applications	283
8.5.1	Absolute Configuration and Detailed Structural Parameters	283
8.5.2	Solution Structure of Biomolecules	287
8.5.3	Supramolecular Systems	292
8.6	Concluding Remarks	299
	Abbreviations	299
	References and Notes	300
9	Crystallography and Crystal Engineering	305
	<i>Kari Rissanen</i>	
9.1	Introduction	305
9.2	Crystallography	306
9.2.1	Introduction	306
9.2.2	A Walk through a Single Crystal Structural Determination	308
9.2.2.1	The (Single) Crystal	309
9.2.2.2	Mounting of the Crystal	310
9.2.2.3	Unit Cell Determination and Preliminary Space Group Selection	312
9.2.2.4	Data Collection, Data Processing and Final Space Group Determination	318
9.2.2.5	Data Reduction, Structure Solution and Refinement	322
9.2.2.6	Analysis of Structure	327
9.3	Crystal Engineering	331
9.3.1	Introduction	331
9.3.2	Definition	331
9.4	Conclusions	334
	Acknowledgements	335
	References and Notes	335
10	Scanning Probe Microscopy	337
	<i>B. A. Hermann</i>	
10.1	Introduction: What is the Strength of Scanning Probe Techniques?	337
10.2	How do Scanning Probe Microscopes Work?	339
10.2.1	Scanning Tunneling Microscopy (STM)	341
10.2.1.1	Working Principle of STM	341
10.2.1.2	Operation Modes of STM	344
10.2.1.3	Imaging with STM	346
10.2.1.4	Tunneling Spectroscopy	350
10.2.1.5	Manipulating Atoms and Molecules with STM	359
10.2.2	Atomic Force Microscopy (AFM)	363
10.2.2.1	Function Principle of AFM	363
10.2.2.2	Various Operation Modes of AFM	364
10.2.2.3	Single Molecule Force Spectroscopy – Force-Distance Measurements	367
10.3	Which Molecules can be Studied?	369
10.3.1	Differences between STM and AFM	370

10.3.2	Exemplary Results on Smaller Molecules	371
10.4	What Results have been Obtained in the Field of Supramolecular Chemistry?	374
10.4.1	Coronenes, Crown ethers, Cryptands, Macrocycles, Squares, Rectangles	375
10.4.2	Calixarenes, Cyclodextrins, Molecular Sieves and Boxes	378
10.4.3	Porphyryns and Phorphyrin Oligomers	380
10.4.4	Complex Interconnected Supermolecules: Rotaxanes and Catenanes	382
10.4.5	Supramolecular Assemblies, Grids, Arrays, Chains	382
	Acknowledgements	384
	References	384
11	The Characterization of Synthetic Ion Channels and Pores	391
	<i>Stefan Matile and Naomi Sakai</i>	
11.1	Introduction	391
11.2	Methods	392
11.2.1	Planar Bilayer Conductance	394
11.2.2	Fluorescence Spectroscopy with Labeled Vesicles	396
11.2.3	Miscellaneous	398
11.3	Characteristics	399
11.3.1	pH Gating	399
11.3.2	Concentration Dependence	400
11.3.3	Size Selectivity	402
11.3.4	Voltage Gating	403
11.3.5	Ion Selectivity	404
11.3.6	Blockage and Ligand Gating	407
11.3.7	Miscellaneous	410
11.4	Structural Studies	412
11.4.1	Binding to the Bilayer	413
11.4.2	Location in the Bilayer	414
11.4.3	Self-Assembly	414
11.4.4	Molecular Recognition	415
11.5	Concluding Remarks	415
	Acknowledgement	416
	References	416
12	Theoretical Methods for Supramolecular Chemistry	419
	<i>Barbara Kirchner and Markus Reiher</i>	
12.1	Introduction	419
12.2	A Survey of Theoretical Methods	422
12.2.1	First-principles Methods	424
12.2.2	The Supramolecular Approach and Total Interaction Energies	430
12.2.3	The Time Dimension: Molecular Dynamics	433
12.2.4	A Technical Note: Linear Scaling and Multiscale Modeling	437

12.2.5	How to Make the Connection to Experiment?	439
12.3	Standard Classification of Intermolecular Interactions	443
12.3.1	A Complication: Cooperative Effects	445
12.3.2	Distributed Multipoles and Polarizabilities	446
12.3.3	Local Multipole Expansions in MD Simulations	447
12.4	Qualitative Understanding and Decomposition Schemes	450
12.4.1	Interaction Energy Decomposition	451
12.4.2	A Core-electron Probe for Hydrogen Bond Interactions	452
12.4.3	The SEN Approach to Hydrogen Bond Energies	452
12.5	General Mechanism for a Static, Step-wise View on Host–Guest Recognition	455
12.5.1	Template-free Pre-orientation Processes	457
12.5.2	Rearrangement Reactions	458
12.5.3	The Host-controlled Association Reaction	459
12.5.4	The Transformation Step	460
12.5.5	Inclusion of Environmental Effects	460
12.5.6	General Aspects of Template Thermodynamics and Kinetics	460
12.6	Conclusions and Perspective	462
	Acknowledgments	463
	References and Notes	463
	Index	472