

Contents

Preface to the first edition — VII

Preface to the second edition — IX

Questions — XVII

1 Introduction and overview — 1

Bibliography — 6

2 Analyzing complex formation — 7

2.1 Thermodynamic and kinetic aspects — 7

2.2 Analytical strategies and techniques — 17

2.2.1 Strategies — 17

2.2.2 NMR spectroscopy — 23

2.2.3 UV-vis spectroscopy — 27

2.2.4 Fluorescence spectroscopy — 29

2.2.5 Potentiometry — 30

2.2.6 Isothermal titration calorimetry — 32

Bibliography — 35

3 Understanding molecular recognition — 37

3.1 Modes of binding — 37

3.1.1 General considerations — 37

3.1.2 Ion-ion interactions — 39

3.1.3 Ion-dipole interactions — 42

3.1.4 Dipole-dipole interactions — 44

3.1.5 Hydrogen bonding — 45

3.1.6 Halogen bonding — 52

3.1.7 Chalcogen bonding — 55

3.1.8 Cation- π interactions — 57

3.1.9 Anion- π interactions — 60

3.1.10 Aromatic interactions — 62

3.1.11 Dispersion interactions — 64

3.2 Binding energies — 66

3.2.1 General considerations — 66

3.2.2 Trend analyses — 67

3.2.3 Double-mutant cycles — 69

3.2.4 Molecular balances — 71

3.3 Solvent effects — 72

3.4 Predicting binding strength in solution — 80

- 3.5 Guidelines for receptor design — **85**
- 3.5.1 Complementarity, preorganization, and induced fit — **85**
- 3.5.2 Chelate effect and macrocyclic effect — **87**
- 3.5.3 Multivalency and cooperativity — **89**
- 3.5.4 Allosterism and cooperativity — **93**
- Bibliography — **97**

4 Hosting ions and molecules — 101

- 4.1 Receptors — **101**
 - 4.1.1 Crown ethers — **101**
 - 4.1.2 Cryptands — **112**
 - 4.1.3 Spherands — **119**
 - 4.1.4 Cyclodextrins — **122**
 - 4.1.5 Cyclophanes — **135**
 - 4.1.6 Cyclotrimeratrylenes — **142**
 - 4.1.7 Calixarenes — **150**
 - 4.1.8 Calixpyrroles — **161**
 - 4.1.9 Resorcinarenes — **164**
 - 4.1.10 Pillararenes — **180**
 - 4.1.11 Cucurbiturils — **187**
 - 4.1.12 Clefts and tweezers — **198**
 - 4.1.13 Foldamers — **207**
- 4.2 Substrates — **211**
 - 4.2.1 Inorganic and organic cations — **212**
 - 4.2.2 Inorganic and organic anions — **214**
 - 4.2.3 Zwitterions and ion pairs — **220**
 - 4.2.4 Neutral organic molecules — **223**
 - Bibliography — **226**

5 Assembling molecules — 235

- 5.1 Self-assembly and template effects — **235**
- 5.2 Self-assembly mediated by the hydrophobic effect — **251**
- 5.3 Self-assembly mediated by hydrogen bonds — **255**
 - 5.3.1 Introduction — **255**
 - 5.3.2 Rosettes — **259**
 - 5.3.3 Capsules — **267**
 - 5.3.4 Tubes — **277**
- 5.4 Self-assembly mediated by halogen and chalcogen bonds — **282**
 - 5.4.1 Introduction — **282**
 - 5.4.2 Helices — **283**

5.4.3	Capsules — 284
5.5	Self-assembly mediated by coordinate bonds — 286
5.5.1	Introduction — 286
5.5.2	Helices — 289
5.5.3	Grids — 294
5.5.4	Rings — 296
5.5.5	Cages — 299
5.6	Self-assembly mediated by covalent bonds — 312
5.6.1	Introduction — 312
5.6.2	Rings — 315
5.6.3	Cages — 320
5.7	Dynamic combinatorial chemistry — 326
5.7.1	Introduction — 326
5.7.2	Casting — 333
5.7.3	Molding — 335
5.7.4	Self-assembly — 339
5.8	Systems chemistry — 342
	Bibliography — 344
6	Making polymers — 353
6.1	Supramolecular polymerization — 353
6.1.1	Isodesmic supramolecular polymerization — 358
6.1.2	Ring-chain supramolecular polymerization — 361
6.1.3	Cooperative supramolecular polymerization — 365
6.1.4	Kinetic aspects — 368
6.2	Reversible interactions within polymer chains — 370
6.2.1	Supramolecular polymerization mediated by hydrogen bonds — 370
6.2.2	Supramolecular polymerization mediated by coordinate bonds — 374
6.2.3	Supramolecular polymerization mediated by aromatic interactions — 376
6.2.4	Supramolecular polymerization mediated by host-guest interactions — 378
6.3	Reversible interactions between polymer chains — 381
	Bibliography — 385
7	Threading molecules — 389
7.1	Molecular topology — 389
7.2	Stereochemical aspects — 394
7.3	Synthetic strategies — 396
7.3.1	Molecular strategies — 396
7.3.2	Supramolecular strategies — 400
7.4	Syntheses using metal coordination — 404

7.4.1	Catenanes — 404
7.4.2	Knots — 411
7.4.3	Rotaxanes — 416
7.5	Syntheses using charge-transfer interactions — 419
7.5.1	Catenanes — 419
7.5.2	Rotaxanes — 424
7.6	Syntheses using hydrogen bonds — 425
7.6.1	Catenanes — 425
7.6.2	Knots — 433
7.6.3	Rotaxanes — 435
7.7	Syntheses using halogen bonds — 438
7.7.1	Rotaxanes — 438
7.8	Syntheses using the hydrophobic effect — 440
7.8.1	Knots — 440
7.8.2	Rotaxanes — 443
	Bibliography — 444
8	Controlling molecular motion — 449
8.1	Introduction — 449
8.2	Rotaxane-derived machines — 461
8.3	Catenane-derived machines — 471
8.4	Machines without mechanical bonds — 475
	Bibliography — 483
9	Mediating molecular transformations — 487
9.1	Introduction — 487
9.2	Stoichiometric transformations — 495
9.2.1	Transformation by functional group participation — 495
9.2.2	Transformation by confinement — 498
9.3	Catalytic transformations — 504
9.3.1	Transformation by functional group participation — 504
9.3.2	Transformation by confinement — 517
9.4	Self-replication — 521
	Bibliography — 530
10	Transporting molecules — 535
10.1	Introduction — 535
10.2	Cation transport — 539
10.2.1	Channels — 539
10.2.2	Carriers — 542
10.3	Anion transport — 545
10.3.1	Channels — 545

10.3.2	Carriers —	547
10.4	Water transport —	550
	Bibliography —	552
11	Detecting molecules —	555
11.1	Introduction —	555
11.2	Single analyte sensing —	557
11.2.1	Direct optical sensing —	557
11.2.2	Indirect optical sensing —	563
11.2.3	Direct electrochemical sensing —	566
11.3	Multi-analyte sensing —	568
	Bibliography —	573
12	Applying supramolecular systems —	575
12.1	Introduction —	575
12.2	Applications in medicine —	576
12.2.1	Drugs —	576
12.2.2	Drug formulations —	579
12.2.3	Sensing —	580
12.2.4	Imaging —	582
12.3	Applications in separation processes —	584
12.3.1	Chromatography —	584
12.3.2	Adsorption —	585
12.3.3	Extraction —	586
12.3.4	Precipitation —	590
12.4	Applications in materials chemistry —	592
12.5	Applications in catalysis —	595
12.6	Applications in molecular electronics —	597
12.7	Applications in consumer products —	598
12.7.1	Textiles —	598
12.7.2	Food —	599
12.7.3	Household —	599
	Bibliography —	600
13	Appendices —	605
13.1	Concentrations in a 1:2 binding equilibrium —	605
13.2	Concentrations in an indicator displacement assay —	606
13.3	Python scripts —	608
13.3.1	Binding isotherm of 1:1 complex formation —	608
13.3.2	Job plot of a 1:1 complex —	609
13.3.3	Binding isotherm of 1:2 complex formation —	610
13.3.4	Job plot of a 1:2 complex —	612

13.3.5	ITC binding isotherm of 1:1 complex formation — 613
13.3.6	Binding isotherm of dimerization — 615
13.3.7	Binding isotherm of isodesmic supramolecular polymerization — 616
13.3.8	Number and weight average degrees of polymerization of isodesmic supramolecular polymerization — 617
13.3.9	Binding isotherm of ring-chain supramolecular polymerization — 618
13.3.10	Number average degree of polymerization of ring-chain supramolecular polymerization — 620
13.3.11	Binding isotherm of cooperative supramolecular polymerization — 622
13.3.12	Number average degree of polymerization of cooperative supramolecular polymerization — 623
	Bibliography — 624

Index — 625