

Fritz Vögtle, Gabriele Richardt and Nicole Werner

Dendrimer Chemistry



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

Contents

Preface XI

1	Introduction	1
1.1	Historical – Cascade molecules and dendrimers	1
1.2	Dendritic architectures	7
1.3	Perfection, defects, dispersity	13
1.4	Definition and classification of dendritic molecules	15
1.5	Nomenclature of dendritic molecules	16
1.5.1	Newkome nomenclature	16
1.5.2	Cascadane nomenclature	17
	Bibliography and Notes for Chapter 1 “Introduction”	22
2	Synthetic methods for dendritic molecules	25
2.1	Divergent synthesis	25
2.2	Convergent synthesis	27
2.3	Recent synthetic methods	28
2.3.1	Orthogonal synthesis	28
2.3.2	Double-stage convergent method	29
2.3.3	Double-exponential method	29
2.3.4	Hypermonomer method	30
2.3.5	Click chemistry	31
2.4	Solid phase synthesis	31
2.5	Coordination-chemical synthesis	33
2.5.1	Metal complex as core unit	33
2.5.2	Metal complexes as branching unit	34
2.6	Supramolecular synthesis	35
2.7	Hyperbranched polymers	38
2.8	Dendronised linear polymers	39
2.8.1	Polymer-analogous method	39
2.8.2	Macromonomer method	41
2.9	Dendro-Isomers	42
	Bibliography and Notes for Chapter 2 “Synthetic methods for dendritic molecules”	44

3	Functional dendrimers	49
3.1	Monofunctional dendrimers	50
3.1.1	Functional core	50
3.1.2	Functional periphery	51
3.1.2.1	Functionalisation of terminal groups	52
3.1.2.2	Introduction of peripheral groups prior to dendrimer growth	54
3.1.3	Functional units in the dendrimer scaffold	55
3.1.3.1	Modification prior to dendrimer growth	55
3.1.3.2	Internal modification on conclusion of dendrimer growth	58
3.2	Multifunctional dendrimers	61
3.2.1	Bifunctionalised molecular periphery	62
3.2.2	Two different functional units in different parts of the molecule	67
3.2.3	More than two different functional units	67
3.2.4	Overview of functional dendrimers and their synthesis	71
	Bibliography and Notes for Chapter 3 "Functional dendrimers"	75
4	Types of dendrimers and their syntheses	81
4.1	Achiral dendrimers	81
4.1.1	POPAM	81
4.1.2	PAMAM	85
4.1.3	POMAM	89
4.1.4	Polylysine dendrimers	90
4.1.5	Dendritic hydrocarbons	93
4.1.5.1	Condensed arene components – Iptyceness	93
4.1.5.2	Dendrimers from arene and multiply bonded building blocks	93
4.1.5.3	Stilbenoid dendrimers	97
4.1.5.4	Hyperbranched polybenzenes	102
4.1.6	Carbon/oxygen-based (and Fréchet) dendrimers	102
4.1.6.1	Polyether dendrimers	102
4.1.6.2	Polyester dendrimers	104
4.1.6.3	Carbohydrate dendrimers (glycodendrimers)	108
4.1.7	Porphyrin-based dendrimers	109
4.1.8	Ionic dendrimers	111
4.1.8.1	Polyanionic dendrimers	111
4.1.8.2	Polycationic dendrimers	114
4.1.9	Silicon-based dendrimers	118
4.1.9.1	Silane dendrimers	118
4.1.9.2	Carbosilane dendrimers	120
4.1.9.3	Carbosiloxane dendrimers	123
4.1.9.4	Siloxane dendrimers	127
4.1.9.5	Hyperbranched silicon-based polymers	128
4.1.10	Phosphorus-based dendrimers	130
4.1.11	Metallodendrimers (and Newkome dendrimers)	133
	Bibliography and Notes for Section 4.1 "Achiral dendrimers"	138
4.2	Chiral dendrimers	143

4.2.1	Classification of chiral dendrimers	143
4.2.2	Studies on the chirality of dendritic molecules	145
4.2.2.1	Chiroptical studies	145
4.2.2.2	Possible applications of chiral dendrimers	146
4.2.3	Dendrimers with chiral core and achiral branching scaffold	146
4.2.3.1	Chiroptical studies on dendrimers with chiral cores	147
4.2.3.2	Possible applications of chiral-core dendrimers	153
4.2.4	Dendrimers with chiral building blocks as spacers or branching units	156
4.2.4.1	Chiroptical studies on dendrimers with chiral dendrimer scaffold	156
4.2.4.2	Possible applications of dendrimers with chiral branching scaffold	158
4.2.5	Chirality in the periphery	158
4.2.5.1	Chiroptical studies on dendrimers with peripheral chiral units	158
4.2.5.2	Possible applications of dendrimers with peripheral chiral units	160
4.2.6	Chiral dendrimers for asymmetric catalysis	161
4.2.7	Interpretation of the chirality of dendritic molecules	161
	Bibliography and Notes for Section 4.2 "Chiral Dendrimers"	165
5	Photophysical properties of dendritic molecules	169
5.1	Luminescence and energy transfer	169
5.1.1	Luminescence	169
5.1.2	Energy transfer	172
5.1.2.1	Dexter mechanism: Energy transfer by radiative emission	172
5.1.2.2	Förster mechanism: Energy transfer by dipole-dipole interactions	172
5.1.2.3	Examples from the field of dendritic molecules	173
5.2	Antenna effect and photoisomerisation of dendrimers	176
5.2.1	Antenna effect	176
5.2.2	Photoisomerisation	186
	Bibliography and Notes for Chapter 5	
	"Photophysical properties of dendritic molecules"	192
6	(Special) chemical reactions of dendritic molecules	195
6.1	Covalent chemical reactions	195
6.1.1	Metathesis	195
6.1.2	Molecular imprinting	201
6.1.3	Covalent introduction of functionalities in the interior of dendritic molecules	203
6.2	Supramolecular (host/guest) interactions	204
6.2.1	Non-covalent modification of a dendrimer periphery	204
6.2.2	Self-assembly of dendrimers	207
6.2.3	Inclusion of guest species in dendritic host molecules	207

- 6.2.3.1 Dendrimers with multiple receptor units 207
- 6.2.3.2 Guest inclusion by steric compression 212
- 6.2.3.3 Guest inclusion by dynamic processes (diffusion) 214
- 6.2.4 Self-assembly of dendrimers 217
- 6.2.5 Dendritic stopper groups (in rotaxanes) 220
- 6.3 Dendritic effects 221
- 6.3.1 Dendritic effect on inclusion of guests 223
- 6.3.2 Dendritic effects in catalysis 224
- 6.3.2.1 Metal-containing dendritic catalysts 224
- 6.3.2.2 Metal-free dendritic catalysts 234
- 6.3.3 Dendritic effects on electrochemical properties 240
- 6.3.3.1 Metal-free dendritic catalysts 240
- 6.3.3.2 Redox gradients 242
- 6.3.3.3 Redox sensors 243
- 6.3.3.4 Redox potential and redox transfer kinetics 244
- 6.3.3.5 Charge-separation processes 244
- 6.3.4 Summary of the dendritic effect 244
- Bibliography and Notes for Chapter 6
- “(Special) chemical reactions of dendritic molecules” 246

- 7 Characterisation and analysis 253**
- 7.1 Chromatography 253
- 7.1.1 Liquid chromatography 253
- 7.1.1.1 Preparative liquid chromatography 254
- 7.1.1.2 High-performance liquid chromatography 254
- 7.1.2 Gel permeation chromatography 257
- 7.2 Gel electrophoresis 259
- 7.3 NMR spectroscopy 260
- 7.3.1 (1D)-NMR spectroscopic studies 261
- 7.3.2 Multidimensional NMR spectroscopy in dendrimer research 261
- 7.3.3 Diffusion NMR spectroscopy 262
- 7.3.4 Dynamic NMR spectroscopy 263
- 7.4 Mass spectrometry 263
- 7.4.1 Gentle ionisation methods: MALDI and ESI 263
- 7.4.1.1 Study of dendrimers by MALDI and ESI-MS 264
- 7.5 X-ray crystal structure analysis 266
- 7.6 Small-angle scattering 266
- 7.6.1 Principle of small-angle scattering 267
- 7.6.2 Capability of small-angle scattering 267
- 7.6.3 Structural analysis of dissolved dendrimers with SANS and SAXS 268
- 7.6.3.1 Radial segment density distribution of flexible dendrimers 268
- 7.6.3.2 Distribution of end groups 269
- 7.6.3.3 Intermolecular interactions of flexible dendrimers in solution 270
- 7.7 Scanning probe microscopy 271

7.7.1	STM and AFM	271
7.7.1.1	AFM images of dendrimers	273
7.7.1.2	STM images of dendrimers	274
7.8	Transmission electron microscopy	274
7.8.1	TEM	274
7.8.1.1	TEM images of dendrimers	275
7.9	Chiroptical methods	276
7.9.1	Optical rotatory dispersion and circular dichroism	277
7.9.2	Chiroptical studies on chiral dendritic structures	279
7.10	Summary	280
	Bibliography and Notes for Chapter 7	
	“Characterization and analysis”	282
8	Special properties and potential applications	289
8.1	Introduction	289
8.2	Catalysis, membrane technology	290
8.2.1	Dendrimers as catalyst supports	291
8.2.2	Catalytic dendrimers for membrane reactors	292
8.2.3	Dendrimers in enantioselective catalysis	293
8.2.4	Dendrimers as phase transfer catalysts	294
8.3	Pigments, adhesives, additives in chemical materials	294
8.3.1	Dendrimers as additives	294
8.3.2	Dendritic polymers for printing inks	295
8.3.3	Dendritic polymers for paints	295
8.3.4	Dendritic polymers as additives in foam formulation	295
8.3.5	Network precursors for plastics	296
8.3.6	Dendrimers as nanocapsules for dyes and for molecular imprinting	296
8.4	Dendrimers for displays and (opto)electronics	298
8.4.1	Liquid-crystalline dendrimers	299
8.5	Biomimetics, sensor technology, diagnostics (fluorescence)	300
8.5.1	Protein dendrimers	300
8.5.2	Glycomimetics	302
8.5.3	Dendrimers in sensor technology	304
8.5.3.1	Quartz micro balance with dendritic sensor layers	304
8.5.3.2	Luminescent dendrimers as sensor materials	306
8.5.3.3	Fluorescing PET sensors	308
8.6	Dendrimers in medical diagnostics	311
8.6.1	Magnetic resonance imaging (MRI) processes	311
8.6.2	DNA dendrimers as biosensors for DNA hybridisation	313
8.7	Medical applications	313
8.7.1	Dendrimers as carriers for cytostatic agents	313
8.7.2	Gene therapy	315
8.7.3	Photodynamic therapy	316

8.7.4	Dendrimers in prevention against HIV	317
8.7.5	Culture of organs and tissue	318
8.7.5.1	Wound healing	318
8.7.6	Boron neutron capture therapy	319
8.8	Dendrimers in nanotechnology	320
8.8.1	Photoswitchable dendrimers	320
8.8.2	Dendrimers as impellers	320
8.8.3	Dendrimers as nanotubes	321
8.8.4	Dendritic polymers as templates	324
	Bibliography and Notes for Chapter 8	
	“Special properties and potential applications”	324

Outlook 331

Subject Index 333