

LIST OF FIGURES

Chapter 1

Figure 1.1. a) Complementary base pairing in DNA helical structure and b) base pairing in DNA (guanine and cytosine form triple hydrogen bonds; adenine and thymine form double hydrogen bonds)	2
Figure 1.2. Electron micrograph of the tobacco mosaic virus	3
Figure 1.3. Self-assembly of the tobacco mosaic virus at different stages	4
Figure 1.4. Model of α helix. Hydrogen bond interactions are denoted by dotted lines	4
Figure 1.5. Models of β -pleated sheets. Side-chains are omitted for clarity. a) The antiparallel β -pleated sheet and b) the parallel β -pleated sheet. Hydrogen bonding interactions are denoted by dotted lines	5
Figure 1.6. The crystal structure of the 1:1 complex of cyanuric acid and melamine	7
Figure 1.7. Complex 3 formed from 1 and 2	7
Figure 1.8. Molecular structures of 4 , 5 , and 6 and their cartoon representations using balls, strings, and rods. Black and white balls denote melamine and cyanuric acid units, respectively. Strings and rods denote flexible and rigid bridging units, respectively	8
Figure 1.9. Molecular structures of 7 and 8 and the X-ray structures of the corresponding dimers 7-7 and 8-8 . Hydrogen bondings are denoted by dotted lines	9
Figure 1.10. Structural representation of the cyclic hexamers 11 assembled from 9 and 10	10
Figure 1.11. Formation of the pseudorotaxane 14 between 12 and 13	11
Figure 1.12. Formation of the pseudorotaxane 17 between 15 and 16	12
Figure 1.13. Formation of the pseudorotaxane 19 between 15 and 18	12
Figure 1.14. Formation of the pseudorotaxane 22 between 20 and 21	13
Figure 1.15. Metal directed synthesis of the catenane 25	14
Figure 1.16. Metal directed synthesis of the molecular knot 28	15
Figure 1.17. Synthesis of the nanocage 31	16

Figure 1.18. Synthesis of the molecular necklace 34	17
Figure 1.19. Synthesis of the fourth generation self-assembling dendrimer 36 from six units of 35 . The dendron wedges in 36 are omitted for clarity	18
Figure 1.20. Construction of nanotubes 38 from cyclic peptides 37	19
Figure 1.21. Synthesis of the main-chain polypseudorotaxane 41	20
Figure 1.22. Synthesis of the main-chain polypseudorotaxane 44	21
Figure 1.23. Self-assembly of thermotropic liquid crystalline polymers 47	22
Figure 1.24. Electron micrographs of supramolecular polymers from the mixture a) <i>LP</i> + <i>LU</i> , b) <i>DP</i> + <i>DU</i> , and c) <i>mP</i> + <i>mU</i>	22
Figure 1.25. Self-assembly of lyotropic liquid crystalline polymer 50	23
Figure 1.26. Self-assembly of side-chain liquid crystalline polymer 53	24
Figure 1.27. Self-assembly of polymeric network 56 and ladder structures 57	25
Figure 1.28. Self-assembly of supramolecular polymers 60 and 61	27

Chapter 2

Figure 2.1. The synthetic routes to 4	36
Figure 2.2. Two-step syntheses of 8 and 11	37
Figure 2.3. The ¹ H NMR spectrum of 8 (400 MHz, chloroform- <i>d</i> , 22°C)	38
Figure 2.4. The ¹ H NMR spectrum of 11 (400 MHz, acetone- <i>d</i> ₆ , 22°C)	39
Figure 2.5. The syntheses of monosubstituted 24- and 25-crown-8 derivatives	40
Figure 2.6. The syntheses of monosubstituted 32-crown-10 derivatives	41
Figure 2.7. The syntheses of difunctionalized 32-crown-10 derivatives	42

Chapter 3

Figure 3.1. Synthesis of 4	56
Figure 3.2. Construction of the 1:3 complex (5)	57
Figure 3.3. The aliphatic region of ¹ H NMR spectrum of solutions of 4 and DB24C8 (1.0 x 10 ⁻² /3.0 x 10 ⁻² M) (400 MHz, acetone- <i>d</i> ₆ , 22°C)	59
Figure 3.4. The aliphatic region of the COSY spectrum of solutions of 4 and DB24C8 (1.0 x 10 ⁻² /3.0 x 10 ⁻² M) (400 MHz, acetone- <i>d</i> ₆ , 22°C)	60

Figure 3.5. Representation of the complexation site between the ammonium salt moiety of 4 and DB24C8	60
Figure 3.6. The aromatic region ^1H NMR spectrum of solutions of 4 and DB24C8 ($1.0 \times 10^{-2}/3.0 \times 10^{-2}$ M) (400 MHz, acetone- d_6 , 22°C)	61
Figure 3.7. The aromatic region of the COSY spectrum of solutions of 4 and DB24C8 ($1.0 \times 10^{-2}/3.0 \times 10^{-2}$ M) (400 MHz, acetone- d_6 , 22°C)	62
Figure 3.8. The stacked ^1H NMR spectra of a 1.0×10^{-2} M solution of 4 mixed with a) 0, b) 1.0×10^{-2} , c) 2.0×10^{-2} , d) 3.0×10^{-2} , e) 4.0×10^{-2} , f) 5.0×10^{-2} , g) 6.0×10^{-2} , and h) 9.0×10^{-2} M solution of DB24C8 (400 MHz, acetone- d_6 , 22°C)	64
Figure 3.9. Representation of the H_{du} and H_{eu} protons in the 1:1 complex	65
Figure 3.10. Representation of the H_{du} and H_{eu} protons in the 1:2 complex	65
Figure 3.11. Synthesis of the deuterated homotritopic molecule 9	66
Figure 3.12. The ^1H NMR spectra of a 1.0×10^{-2} M solution of a) 4 and b) 9 (400 MHz, acetone- d_6 , 22°C)	67
Figure 3.13. The stacked ^1H NMR spectra of a 1.0×10^{-2} M solution of 9 mixed with a) 0, b) 1.0×10^{-2} , c) 2.0×10^{-2} , d) 3.0×10^{-2} , e) 4.0×10^{-2} , and f) 9.0×10^{-2} solution of DB24C8 (400 MHz, acetone- d_6 , 22°C)	68
Figure 3.14. The FAB mass spectrum of the 1:3 complex	69
 Chapter 4	
Figure 4.1. Cartoon representations of triply charged ammonium salt 1 and dibenzyl ammonium hexafluorophosphate 2	75
Figure 4.2. Cartoon representations of 3 , 4 , and 5	77
Figure 4.3. Illustrations of the construction of a series of self-assembling dendritic pseudorotaxanes from complementary building blocks	78
Figure 4.4. The aliphatic region of stacked ^1H NMR spectra of a) a 3.0×10^{-2} M solution of 1st generation dendron 3 and a 3.0×10^{-2} M solution of 3 mixed with 1/3 mol equivalent of solid 1 after b) 10 min and c) 15 h (400 MHz, chloroform- d , 22°C)	79
Figure 4.5. The designation of the benzylic protons in 1 and 3 for the signal assignments	80

- Figure 4.6.** The aromatic region of stacked ^1H NMR spectra of a) a 3.0×10^{-2} M solution of **3** and a 3.0×10^{-2} M solution of **3** mixed with 1/3 mol equivalent of solid **1** after b) 10 min and c) 15 h (400 MHz, chloroform-*d*, 22°C) 81
- Figure 4.7.** The aliphatic region of stacked ^1H NMR spectra of a) a 3.0×10^{-2} M solution of 3rd generation dendron **5** and a 3.0×10^{-2} M solution of **5** mixed with 1/3 molar equivalent of solid **1** recorded after b) 10 min., and c) 72 h (400 MHz, chloroform-*d*, 22°C) 83
- Figure 4.8.** The designation of the benzylic protons in **1** and **5** for the signal assignments 84
- Figure 4.9.** The aromatic region of stacked ^1H NMR spectra of a) a 3.0×10^{-2} M solution of **5** and a 3.0×10^{-2} M solution of 3rd generation dendron **5** mixed with 1/3 molar equivalent of solid **1** recorded after b) 10 min., and c) 72 h (400 MHz, chloroform-*d*, 22°C) 85
- Figure 4.10.** The aliphatic region of stacked ^1H NMR spectra of solutions of **1** and 1st generation dendron **3** at a) $0/1.0 \times 10^{-2}$, b) $1.0 \times 10^{-2}/0$, c) $1.0 \times 10^{-2}/1.0 \times 10^{-2}$, d) $1.0 \times 10^{-2}/3.0 \times 10^{-2}$, e) $1.0 \times 10^{-2}/4.0 \times 10^{-2}$, f) $1.0 \times 10^{-2}/5.0 \times 10^{-2}$, and g) 1.0×10^{-2} M/ 6.0×10^{-2} M (400 MHz, acetone-*d*₆, 22°C) 87
- Figure 4.11.** The aliphatic region of stacked ^1H NMR spectra of solutions of **1** and 2nd generation dendron **4** at a) $0/1.0 \times 10^{-2}$, b) $1.0 \times 10^{-2}/0$, c) $1.0 \times 10^{-2}/1.0 \times 10^{-2}$, d) $1.0 \times 10^{-2}/2.0 \times 10^{-2}$, e) $1.0 \times 10^{-2}/3.0 \times 10^{-2}$, f) $1.0 \times 10^{-2}/4.0 \times 10^{-2}$, g) $1.0 \times 10^{-2}/5.0 \times 10^{-2}$, and h) 1.0×10^{-2} M/ 6.0×10^{-2} M (400 MHz, acetone-*d*₆, 22°C) 89
- Figure 4.12.** The aliphatic region of stacked ^1H NMR spectra of solutions of **1** and 3rd generation dendron **5** at a) $0/1.0 \times 10^{-2}$, b) $1.0 \times 10^{-2}/0$, c) $1.0 \times 10^{-2}/1.0 \times 10^{-2}$, d) $1.0 \times 10^{-2}/2.0 \times 10^{-2}$, e) $1.0 \times 10^{-2}/3.0 \times 10^{-2}$, f) $1.0 \times 10^{-2}/4.0 \times 10^{-2}$, g) $1.0 \times 10^{-2}/5.0 \times 10^{-2}$, and h) 1.0×10^{-2} M/ 6.0×10^{-2} M (400 MHz, acetone-*d*₆, 22°C) 91
- Figure 4.13.** The FAB mass spectrum of the 1st generation dendrimer **1(3)**₃ 93
- Figure 4.14.** The FAB mass spectrum of the 2nd generation dendrimer **1(4)**₃ 94
- Figure 4.15.** The MALDI-TOF mass spectrum of the 3rd generation dendrimer **1(5)**₃ 95
- Figure 4.16.** The molecular modeling of the 3rd generation dendrimer. The hydrogen atoms are omitted for clarity 97

Chapter 5

- Figure 5.1.** Synthesis of **3a**, **3b**, and **7** 103
- Figure 5.2.** Illustration of the constructions of the supramolecules **8** and **9** from **3a** and **7** 104
- Figure 5.3.** The stacked ^1H NMR spectra of solutions of **3a** and **7** at a) $1.0 \times 10^{-2}/0$, b) $0/1.0 \times 10^{-2}$, and c) 1.0×10^{-3} , d) 1.0×10^{-2} , e) 0.10, f) 0.50, g) 1.0, and h) 2.0 M equimolar solutions (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C). The three sets of signals are for uncomplexed **3a** and **7** (u), **8** (d), and **9** (l) 106
- Figure 5.4.** The stacked ^1H NMR spectra of solutions of **3a** and **7** at a) $1.0 \times 10^{-2}/0$, b) $0/1.0 \times 10^{-2}$, c) $1.0 \times 10^{-2}/1.0 \times 10^{-2}$, d) $2.0 \times 10^{-2}/1.0 \times 10^{-2}$, e) $4.0 \times 10^{-2}/1.0 \times 10^{-2}$, f) $8.0 \times 10^{-2} \text{ M}/1.0 \times 10^{-2} \text{ M}$ (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C). The three sets of signals are for uncomplexed **3a** and **7** (u), **8** (d), and **9** (l) 107
- Figure 5.5.** Reduced viscosity as a function of concentration in acetone/chloroform (1/1, v/v) at 22°C for a) **3b** and **7** and b) **3a** and **7** 110
- Figure 5.6.** DSC traces of a) the 0.50 M sample and b) $1.0 \times 10^{-2} \text{ M}$ sample (2nd heating at 10°C/min) 112
- Figure 5.7.** Longitudinal views of scanning electron micrographs of a fiber pulled from a concentrated acetone/chloroform (1/1, v/v) equimolar solution of **3a** and **7** ($>2.0 \text{ M}$) a) low resolution b) high resolution 113

Chapter 6

- Figure 6.1.** Cartoon illustrations of formation of the linear dimer complex **6** and cyclic dimer complex **7** from homoditopic molecules **1** and **5** in substantially dilute conditions 118
- Figure 6.2.** Complementary homoditopic molecules 119
- Figure 6.3.** Synthetic approach to a series of homoditopic molecules 120
- Figure 6.4.** The stacked ^1H NMR spectra of equimolar solutions of a) **1** and **5a**, b) **1** and **5b**, and c) **1** and **5c** ($4.0 \times 10^{-4} \text{ M}$ each) and d) a solution of DB24C8 and **5b** ($8.0 \times 10^{-4}/4.0 \times 10^{-4} \text{ M}$) at 22°C (400 MHz, acetone- d_6 /chloroform- d , 1/1, v/v) 122
- Figure 6.5.** Cartoon illustrations of the formation of the 1:1 dimer complex **9b** from DB24C8 and homoditopic molecule **5b** in substantially dilute conditions 123

Chapter 7

Figure 7.1. Cartoon illustration of the construction of the supramolecules **3** and **4** from heteroditopic molecules **1** and **2** 132

Figure 7.2. Synthesis of **2d** 133

Figure 7.3. The stacked ^1H NMR spectra of solutions of **1** and **2a** at a) 1.0×10^{-2} /0, b) 0/ 1.0×10^{-2} , c) 1.0×10^{-3} , d) 1.0×10^{-2} , e) 0.1, and f) 0.5 M each (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C). The three sets of signals are for uncomplexed **2a** (u), **3a** (d), and **4a** (l) 134

Figure 7.4. The stacked ^1H NMR spectra of solutions of **1** and **2c** at a) 1.0×10^{-3} , b) 1.0×10^{-2} , c) 0.1, d) 0.5, and e) 1.0 M each (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C). The three sets of signals are for uncomplexed **2c** (u), **3c** (d), and **4c** (l) 136

Figure 7.5. The average number of repeat units, n , in **4** as a function of concentration of **1** and **2** 137

Figure 7.6. The percentages of ammonium salt moieties in cyclic dimer **3** as a function of concentration of **1** and **2** 137

Chapter 8

Figure 8.1. Outline of the synthesis of the heteroditopic molecule **4** 143

Figure 8.2. The ^1H NMR spectrum of **2** (400 MHz, chloroform- d , 22°C) 144

Figure 8.3. The ^1H NMR spectrum of **4** (400 MHz, DMSO- d_6 , 22°C) 145

Figure 8.4. Cartoon representations of the formation of linear arrays **5** and cyclic species **6** by self-assembly of **4** 146

Figure 8.5. The ^1H NMR spectrum of **4** (400 MHz, acetone- d_6 , 22°C) 147

Figure 8.6. The stacked variable-temperature ^1H NMR spectra of equimolar solutions of DB24C8 and dibenzylammonium salt at a) 22, b) 0, c) -20, d) -30, e) -40, f) -50, and g) -60°C (2.0×10^{-2} M each, 400 MHz, acetone- d_6) 149

Figure 8.7. The stacked variable-temperature ^1H NMR spectra of a 2.0×10^{-2} M solution of **4** at a) 22, b) 10, c) 0, d) -20, e) -40, and f) -60°C (400 MHz, acetone- d_6) 151

Figure 8.8. The MALDI spectrum of the solid sample prepared from **4** 153

Figure 8.9. The FAB mass spectrum of the solid sample prepared from **4** 153

Chapter 9

- Figure 9.1.** Illustration of three types of polypseudorotaxanes. **1a** and **1b**: linear main-chain polypseudorotaxanes, **2**: linear side-chain polypseudorotaxanes 158
- Figure 9.2.** Synthesis of the crown ether side-chain polymethacrylate **5** and PMMA (**6**) via polymer precursor **3** 159
- Figure 9.3.** The ^1H NMR spectra in the aliphatic region of solutions (10 mL) of a) **5a** with an insert of the vertically enlarged CH_3O^- signal and b) **5d** (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C) 161
- Figure 9.4.** Cartoon representation of construction of **8** from **5** and **7** 162
- Figure 9.5.** The stacked ^1H NMR spectra in the aliphatic region of solutions **5a** and **7** at a) 0/10, b) 10/0, c) 10/20, and d) 10 mM/40 mM (400 MHz, acetone- d_6 /chloroform- d (1/1, v/v), 22°C) 163
- Figure 9.6.** Plots of fraction complexed in **8** versus concentration of **7**: a) **5a**, b) **5b**, c) **5c**, and d) **5d** vs. **7** (relative error $\leq \pm 6\%$). The initial concentrations of crown ether moieties of polymers **5a-c** and **5d** were 10 mM and 12 mM, respectively 165
- Figure 9.7.** Representation of one possible configurational structure of syndiotactic crown ether side-chain heptamer. The hydrogen atoms are omitted for clarity 166
- Figure 9.8.** Representation of planar zigzag projections of syndiotactic pentad sequences 167
- Figure 9.9.** Possible complexation equilibria of crown ether (at position 3 of pentad structures) with **7** 168
- Figure 9.10.** Longitudinal views of scanning electron micrographs of films prepared by freeze-drying solutions of **5a** and **7** at a) 100/0 and b) 100 mM/20 mM 172

Chapter 10

- Figure 10.1.** Syntheses of the dialkylammonium salts **5a** and **5b** 179
- Figure 10.2.** The ^1H NMR spectrum of **5a** (400 MHz, chloroform- d , 22°C) 180
- Figure 10.3.** The ^1H NMR spectrum of **5a** (400 MHz, chloroform- d , 22°C) 181

Figure 10.4. The stacked ^1H NMR spectra of a) a 2.0×10^{-2} M solution of 5a and b) an equimolar solution of 5a and DB24C8 (2.0×10^{-2} M each) (400 MHz, acetone- d_6 , 22°C)	182
Figure 10.5. The stacked ^1H NMR spectra of a) a 2.0×10^{-2} M solution of 6 and b) an equimolar solution of 6 and DB24C8 (2.0×10^{-2} M each) (400 MHz, acetone- d_6 , 22°C)	183
Figure 10.6. The stacked ^1H NMR spectra of equimolar solutions of 5a and DB24C8 (2.0×10^{-2} M each) recorded after a) 10min, b) 20 hours, c) 40 hours, and d) 73 hours (400 MHz, chloroform- d , 22°C)	186
Figure 10.7. The stacked ^1H NMR spectra of an equimolar solution of 5b and DB24C8 (2.0×10^{-2} M each) recorded after a) 5 min. at 22°C , b) 6 days at 53°C , and c) 11 days at 53°C (400 MHz, chloroform- d)	188
Figure 10.8. The pseudorotaxane complex formed from 5a and DB24C8	189
 Chapter 11	
Figure 11.1. Synthesis of the heteroditopic molecule 3	195
Figure 11.2. The ^1H NMR spectrum of 3 (400 MHz, DMSO- d_6 , 22°C)	196
Figure 11.3. Illustration of the formation of the linear oligo- and polymolecular arrays 5 by self-organization of 3	197
Figure 11.4. The stacked ^1H NMR spectra recorded for 3 at concentrations of a) 2.0, b) 5.0×10^{-1} , c) 5.0×10^{-2} , d) 1.0×10^{-2} , e) 1.0×10^{-3} , f) 5.0×10^{-4} , and g) 6.3×10^{-5} M (400 MHz, acetone- d_6 , 22°C)	199
Figure 11.5. The stacked ^1H NMR spectra of a 1.0×10^{-2} M solution of 5 mixed with a) 0, b) 1.0×10^{-1} , c) 5.0×10^{-1} , d) 1.0, and e) 2.0 M solution of tetrabutyl ammonium hexafluorophosphate (400 MHz, acetone- d_6 , 22°C)	201
Figure 11.6. The ^1H NMR spectra of a) 5 at 2.0 M and b) 1b and 6 (2.0/2.0 M) (400 MHz, acetone- d_6 , 22°C)	202
Figure 11.7. The NOESY spectrum of 5 (400 MHz, acetone- d_6 , 30°C)	204
Figure 11.8. Reduced viscosity as a function of concentration (solutions in acetone at 22°C) a) 5 and b) 1b and 6 (1:1)	205

Figure 11.9. The FAB mass spectrum of the self-organized pseudo-oligomeric material 5	207
Figure 11.10. Longitudinal views of scanning electron micrographs of a fiber pulled from a concentrated acetone solution of 3 (>2.0 M)	208
Figure 11.11. The AFM images of a fiber pulled from a concentrated acetone solution of 3 (>2.0 M) a) height and b) phase	208
Figure 11.12. Roughness analysis of the fiber surface	209
Chapter 12	
Figure 12.1. Cartoon representations of the blocking and slippage approach to mechanically interlocked polymeric materials	215
Figure 12.2. Synthesis of the blocking group	218
Figure 12.3. The ^1H NMR spectrum of 2 (400 MHz, chloroform- <i>d</i> , 22°C)	219
Figure 12.4. Synthesis of heteroditopic molecule 6	221
Figure 12.5. The ^1H NMR spectrum of 6 (400 MHz, DMSO- <i>d</i> ₆ , 22°C)	222
Figure 12.6. Illustration of the model system between 7 and BMP32C10 to form 8	223
Figure 12.7. The stacked ^1H NMR of a) 7 (2.0×10^{-2} M) and b) equimolar solutions of BMP32C10 and 7 (2.0×10^{-2} M each) (400 MHz, acetonitrile- <i>d</i> ₃ , 22°C)	224
Figure 12.8. The stacked ^1H NMR spectra of 6 (3.2×10^{-2} M) recorded after a) 1 day, b) 5 days, c) 17 days, d) 31 days, and e) 37 days (400 MHz, acetonitrile- <i>d</i> ₃ , 22°C)	226
Chapter 13	
Figure 13.1. Cartoon representation of two types of main-chain polypseudorotaxanes	233
Figure 13.2. Self-assembly approach to construct a main-chain polypseudorotaxane of type 1	233
Figure 13.3. Synthesis of model polyester 8	234
Figure 13.4. Synthesis of poly(ester crown ether) 10	235
Figure 13.5. Mechanism of physical cross-linking <i>via</i> intermolecular hydrogen bonding between crown ether monomer molecules	235

Figure 13.6. Synthesis of model polyurethane	236
Figure 13.7. Synthesis of poly(urethane crown ether)	237
Chapter 14	
Figure 14.1. Synthesis of non-covalent network system	243