

Table of contents

| | |
|---------------------------------------------------------------------------------------------|----|
| 1. Introduction | 1 |
| 2. Aim of the work | 7 |
| 3. Literature survey | 10 |
| 3.1. General aspects of synthetic strategies | 10 |
| 3.2. Relevant cases | 17 |
| 3.3. Aggregation of mesogenic compounds with specific emphasis on cylindrical stacks | 32 |
| 3.3.1. Solid state structures in shape persistent macrocycles | 33 |
| 3.3.2. Aggregation of shape persistent macrocycles in solution | 35 |
| 3.4. Ru and Os complexes of bipyridines | 37 |
| 4. General part | 42 |
| 4.1. Retrosynthetic analysis of cycle synthesis | 42 |
| 4.2. Improvements and new building blocks | 44 |
| 4.2.1. Synthesis of side stone A | 44 |
| 4.2.2. Synthesis of side stone D | 49 |
| 4.2.3. Synthesis of quaterphenyl unit 83 | 54 |
| 4.2.4. Synthesis of non-symmetrical bisfunctionalised building block 85 | 55 |
| 4.2.5. Synthesis of corner stone B | 60 |
| 4.2.6. Synthesis of cycle precursors 100b and 100c | 62 |
| 4.2.7. Synthesis of cycle precursor C | 63 |
| 4.3. Ring closure reactions | 66 |
| 4.3.1. Ring closure reactions by Sonogashira-Hagihara cross-coupling of two building blocks | 67 |
| 4.3.1.1. Syntheses of macrocycles 103a-c | 68 |
| 4.3.1.2. Synthesis of macrocycle 10 | 76 |
| 4.3.1.3. Synthesis of the macrocycle 103d | 77 |
| 4.3.2. Ring closure reactions by Sonogashira-Hagihara cross-coupling of one cycle precursor | 82 |

| | |
|-----------------------------------------------------------------------------------------------------|-----|
| 4.3.3. Ring closure reactions by oxidative acetylene coupling | 86 |
| 4.4. Polymerization of macrocycles with pendant polymerizable unit | 94 |
| 4.4.1. Model compounds and reactions | 94 |
| 4.4.2. Macrocycle macromonomers 112a and 112c , and their polymerization | 98 |
| 4.5. Synthesis of Ru and Os complexes | 107 |
| 4.5.1. Synthesis of Os complex 115 | 108 |
| 4.5.2. Ru and Os complex of macrocycle 103c | 110 |
| 4.5.3. Synthesis of the Os complex of macrocycle 10 | 113 |
| 4.5.4. Synthesis of the mixed Ru/Os complex 118 | 117 |
| 4.5.5. Synthesis of model compounds 119a,b and 120 | 121 |
| 4.6. Photophysical and electrochemical investigations | 127 |
| 4.6.1. Photophysical properties of macrocycle 113c and its Ru and Os complexes | 127 |
| 4.6.2. Electrochemical properties of macrocycle 113c and its Ru and Os complexes | 129 |
| 4.6.3. Photophysical properties of macrocycle 10 and its Ru and Os complexes | 131 |
| 4.6.4. Electrochemical properties of macrocycle 10 and its Ru, Os, and mixed Ru/Os complexes | 135 |
| 4.6.5. Photophysical properties of the mixed Ru/Os complex of macrocycle 10 | 139 |
| 4.7. X-ray analysis on single crystals | 147 |
| 4.7.1. Macrocycle 103c | 147 |
| 4.7.2. Macrocycle 106 | 150 |
| 4.8. Liquid crystalline phases of some bipyridine macrocycles | 153 |
| 5. Summary | 159 |
| 6. Zusammenfassung | 161 |
| 7. Experimental part | 163 |
| 7.1. General | 163 |
| 7.2. Syntheses | 164 |

Table of contents

| | |
|----------------------------------|-----|
| 7.2.1. Compounds of Chapter 4.2. | 165 |
| 7.2.2. Compounds of Chapter 4.3. | 193 |
| 7.2.3. Compounds of Chapter 4.4. | 204 |
| 7.2.4. Compounds of Chapter 4.5. | 215 |
| 7.3. Crystallographic data | 224 |
| 8. References | 225 |
| Appendix | 233 |
| Symbols and Abbreviations | 233 |
| List of Publications | 236 |
| Posters and Presentations | 238 |
| Curriculum Vitae | 240 |