

**UNIVERSITÀ DEGLI STUDI DI ROMA “LA SAPIENZA”**



**PhD IN CHEMICAL SCIENCES**

***XXIV CYCLE***

Curriculum: Synthesis and Reactivity

**Synthesis of New Building Blocks for the Construction of  
Self-Assembled Molecular Architectures**

**Supervisor**

Antonella Dalla Cort

**Co-Supervisor**

Laurent Bouteiller

**Co-Supervisor**

Gustavo Portalone

**Candidate**

Ilaria Giannicchi

# **TABLE OF CONTENTS**

<b><u>Outline</u></b>	1
-----------------------	---

## **Chapter 1 - New metal-salophen complexes to build up supramolecular architectures in solution and in solid state**

1.1 Introduction	3
1.1.a Self-assembling	3
1.1.b Aim of the research	7
1.2 Results and discussion	9
1.2.a Synthesis of Zn-salophen complexes using 2,3-diaminopyridine	9
1.2.b Characterisation	11
1.2.c X-ray diffraction	12
1.2.d Synthesis of Zn-salophen complex 9	16
1.2.e Synthesis of Zn-salophen complex 13	18
1.3 Conclusions	19
1.4 Experimental section	19

## **Chapter 2 - Functionalization of self-assembled supramolecular polymers**

2.1 Introduction	26
2.1.a Definition of gel	27
2.1.b Applications and examples of physical gels	28
2.1.c Aim of the research	33
2.2 Results and discussion	35
2.2.a Synthesis of halogenated bis-ureas	35
2.2.b Characterisation	37
2.2.c Solubility and viscosity	38
2.2.d Small Angle Neutron Scattering (SANS)	39
2.2.e Spectroscopy FT-IR	41
2.2.f Isothermal Titration Calorimetry (ITC)	44
2.2.g Synthesis of mono-fluorinated bis-urea	

2.3	Conclusions	53
2.4	Experimental section	54

### **Chapter 3 - Synthesis of new [2]-rotaxanes systems**

3.1	Introduction	60
3.1.a	Definition	60
3.1.b	Method of synthesis	61
3.1.c	Uses of rotaxane systems	63
3.1.d	Aim of the research	66
3.2	Results and discussion	67
3.3	Conclusions	74
3.4	Experimental section	75

### **Chapter 4 - Synthesis and binding studies of new macrocyclic receptors**

4.1	Introduction	81
4.1.a	Contact ion pair	82
4.1.b	Solvent bridged ion pair	84
4.1.c	Host separated ion pair	85
4.1.d	Aim of the research	86
4.1.e	Spectrophotometric titrations	87
4.2	Results and discussion	90
4.2.a	UV-Vis titrations	90
4.2.b	$^1\text{H-NMR}$ titrations on macrocycle A	92
4.3	Conclusions	93

### **Appendix 1**

94