

Dedicated to my parents...

Sudipta Chakraborty

&

Late Pranay Kumar Chakraborty

DECLARATION

I, **Sutapa Chakraborty** bearing Registration No. **Ph.D./1767/11** dated **22.09.2011**, hereby declare that the subject matter of the thesis entitled **“Synthesis, Mesomorphic and Photoluminescence Study of Strategically designed Schiff base ligands and their Complexes with some Transition Metal ions”** submitted to Assam University, Silchar for the partial fulfillment of the degree of Doctor of Philosophy in Chemistry is the record of work done by me and that the contents of this thesis did not form the basis for award of any other degree to me or anybody else to the best of my knowledge. The thesis has not been submitted to any other University/Institute.

Place: Assam University, Silchar

Date: 26/12/2016

Sutapa Chakraborty

Sutapa Chakraborty

Acknowledgements

It gives me immense pleasure to offer my heartfelt thanks to all those who have contributed to this thesis and supported me in one way or the other during this amazing journey.

I owe deepest sense of gratitude to my guide Prof. Chira R. Bhattacharjee who provided me the space and time and shared his valuable experience throughout this entire period. His enthusiasm, integral view on research and endeavor to produce high-quality work, has made a deep impression on me.

My sincere gratitude is reserved for Prof. B. S. Purkayastha, Dean, Albert Einstein School of Physical Sciences, Assam University, for his continuous support.

Thanks are also due to Dr. P. C. Paul, Head, Department of Chemistry, for his invaluable insights and suggestions.

I am thankful to our collaborator, Dr. P. Mondal, Department of Chemistry, for help with the computational analysis. Discussion with Dr. T. S. Singh on some aspect of experimental work have been rather illuminating.

I have had the support and encouragement of Prof. S. B. Paul, Dr. M. K. Paul, Dr. D. Sengupta, Dr. H. Acharya, Dr. S. K. Ghosh, Dr. S. Choudhury and Dr. R. Panchadhayee, faculty members of the Department of Chemistry, Assam University.

I would like to express my gratitude to Prof. Jayashree Rout, Department of Ecology & Environmental Sciences, Assam University for her encouragement and fruitful association.

My heartfelt appreciation also goes to all the research scholars of our group especially Dr. Debraj Dhar Purkayastha, Dr. Gobinda Das, Dr. Mridusmita Mishra, Dr. Chitraniva Datta, Dr. Richa Chaturvedi, Dr. Harun All Rashid Pramanik, Rajat Goswami, Abhijit Nath, Bishop Devgupta, Rupam Chakrabarty and Nirmalendu Das for their continuous support, advice, discussions and encouragement during difficult times by creating wonderful work atmosphere in the lab.

I am indebted to all my colleagues from other research laboratories, especially Sudip Kr. Pal, Hasimur Rahman and Nayan Roy for their manifold help.

Thanks are also due to Dr. Sarmistha Dey, for her continuous support and encouragement and lending generous help in getting the printing job done.

I acknowledge the contribution of technical staffs Mr. P. R. Ramesh, Mr. S. Bhattacharjee, Mr. B. Nath, Mr. A. Barbhuiya and Mr. R. Kurmi. I am equally thankful to Mr. J. A. Barbhuiya and Mr. L. Hmar, office staff of the department for their help throughout.

I would like to offer my special thanks to our collaborators, Dr. D. S. S. Rao and Dr. S. K. Prasad, Centre for Nano and Soft Matter Sciences, Bangalore, for help with variable temperature powder X-ray diffraction measurements. Thanks are also due to SAIF, NEHU Shillong and CDRI Lucknow for spectral facilities.

I gratefully acknowledge the financial assistance received in the form of INSPIRE Research Fellowship (Fellowship code: IF110692) under AORC scheme from Department of Science and Technology (DST), India.

Words would be inadequate to express my deepest sense of reverence to my parents and my elder brother Arindwam whose unconditional love, support and continuous motivation were always by my side. Your constructive comments and warm encouragement were a source of inspiration to me both in good and hard times and saying so I really mean it as "I feel greatly your absence - 'dear dad' to share this moment of glory which I have always longed for". My special thanks to my dear brother for help in compiling this thesis - getting all the job done to near perfection.

"I am forever grateful to Almighty for showering his blessings and wisdom unto me ..."

Sutapa Chakraborty
Sutapa Chakraborty

CONTENTS

		Page no.
ABSTRACT		i–v
CHAPTER 1	GENERAL INTRODUCTION	1–42
1.1	Schiff Base	1
1.2	Metal complexes of Schiff base ligands	3
1.3	Structure and properties of some Schiff base metal complexes	5
1.3.1	Vanadium Schiff base complexes	5
1.3.2	Nickel Schiff base complexes	6
1.3.3	Copper Schiff base complexes	7
1.3.4	Group 12 metals Schiff base complexes:	7
1.4	Application of metal Schiff base complexes	8
1.4.1	Catalysis	8
1.4.2	Biological applications	9
1.4.3	Liquid crystal	10
1.4.4	Photophysical properties of metal Schiff base complexes	28
1.5	Objectives	29
	References	
CHAPTER 2	MATERIALS AND INSTRUMENTAL TECHNIQUES USED	43–45
2.1	Chemicals and solvents	43
2.2	Instrumental techniques used	43
CHAPTER 3	BIDENTATE [N,O]-DONOR SALICYLALDIMINE SCHIFF BASE LIGAND AND ITS MESOMORPHIC AND PHOTOLUMINESCENT TETRAHEDRAL d¹⁰-METAL COMPLEXES	46–70
3.1	Introduction	46
3.2	Experimental	47
3.2.1	Synthesis of ligand	48
3.2.2	Synthesis of zinc(II), cadmium(II) and mercury(II) complexes, [ML ₂] (M = Zn, Cd, Hg)	48
3.3	Results and discussion	50

	3.3.1	Synthesis and structural assessment	50
	3.3.2	Liquid crystalline properties	50
	3.3.3	Photophysical properties	57
	3.3.4	DFT study	59
	3.4	Conclusion	65
		References	
CHAPTER	4	TETRADENTATE [N₂O₂]-DONOR ASYMMETRIC ‘SALEN’ TYPE SCHIFF BASE LIGANDS AND THEIR MESOMORPHIC AND PHOTOLUMINESCENT ZINC(II) COMPLEXES	71–95
	4.1	Introduction	71
	4.2	Experimental	72
	4.2.1	Synthesis of ligands	73
	4.2.2	Synthesis of zinc(II) complexes (Zn-ndap, n=12, 14, 16)	75
	4.3	Results and discussion	76
	4.3.1	Synthesis and structural assessment	76
	4.3.2	Liquid crystalline properties	77
	4.3.3	Photophysical properties	82
	4.3.4	DFT study	87
	4.4	Conclusion	91
		References	
CHAPTER	5	SYNTHESIS, MESOMORPHISM AND PHOTOPHYSICAL PROPERTIES OF TETRADENTATE [N₂O₂]-DONOR ‘SALPHEN’ TYPE SCHIFF BASE LIGANDS AND THEIR VO(IV), Ni(II), Cu(II) AND Zn(II) COMPLEXES	96–191
	5.1	Introduction	96
	5.2	Experimental	97
	5.2.1	Synthesis of salphen ligands	97
	5.2.2	Synthesis of metal complexes (M = VO ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺).	105
	5.3	Results and discussion	116
	5.3.1	Mono-substituted salphen ligands	116

5.3.1.1	Synthesis and structural assessment	116
5.3.1.2	Liquid crystalline properties	117
5.3.1.3	Photophysical properties	122
5.3.1.4	DFT study	125
5.3.2	VO(IV) complexes of mono-substituted salphen ligands; VO-nXpd (X = f, c, b)	127
5.3.2.1	Synthesis and structural assessment	127
5.3.2.2	Liquid crystalline properties	128
5.3.2.3	DFT study	134
5.3.3	Ni(II) complexes of mono-substituted salphen ligands; Ni-nXpd (X = f, c, b)	135
5.3.3.1	Synthesis and structural assessment	135
5.3.3.2	Liquid crystalline properties	136
5.3.3.3	Photophysical properties	144
5.3.4	Cu(II) complexes of mono-substituted salphen ligands; Cu-nXpd (X = f, c, b)	146
5.3.4.1	Synthesis and structural assessment	146
5.3.4.2	Liquid crystalline properties	147
5.3.5	Zn(II) complexes of mono-substituted salphen ligands; Zn-nXpd (X = f, c, b)	148
5.3.5.1	Synthesis and structural assessment	148
5.3.5.2	Liquid crystalline properties	149
5.3.5.3	Photophysical properties	156
5.3.5.4	DFT study	161
5.3.6	Comparative assessment of thermal and photophysical properties of the mono-substituted salphen ligands and corresponding metal complexes	164
5.3.7	Di-substituted salphen ligands and their metal complexes	165
5.3.7.1	Synthesis and structural assessment	165
5.3.7.2	Liquid crystalline properties	167
5.3.7.3	Photophysical properties	174
5.3.7.4	DFT study	182

5.3.8	Comparative assessment of thermal and photophysical properties of the mono-and di-substituted salphen ligands and their metal complexes	183
5.4	Conclusion References	187
CHAPTER 6	SUMMARY	192-193
ANNEXURE I	Pre-Ph.D. Coursework Marksheet	
ANNEXURE II	Reprints of published papers	

LIST OF FIGURES

FIGURE No.	TITLE	Page No.
CHAPTER 1	GENERAL INTRODUCTION	1-42
Fig. 1.1	: Examples of Schiff bases of varied denticities.	2
Fig. 1.2	: Examples of macrocyclic Schiff base ligands.	3
Fig. 1.3	: Hydrogen-bonding interaction in polymeric vanadyl complexes.	6
Fig. 1.4	: Structure of cholesteryl benzoate.	11
Fig. 1.5	: The melting process of a calamitic liquid-crystalline material.	13
Fig. 1.6	: Schematic representation of cholesteric phase.	14
Fig. 1.7	: Schematic representation of SmA(left), SmC(middle) and SmB(right) phases.	15
Fig. 1.8	: Structure of various nematic phases exhibited by discotic mesogens: (a) discotic nematic, (b) chiral nematic, (c) columnar nematic and (d) nematic lateral.	16
Fig. 1.9	: Smectic (discotic lamellar) phase of disc-like mesogens.	17
Fig. 1.10	: Structure of the hexagonal columnar phase.	17
Fig. 1.11	: Structure of different types of rectangular columnar phases.	18
Fig. 1.12	: Structure of the oblique columnar phase.	18
Fig. 1.13	: Structure of the plastic columnar phase. The curved arrow indicates the rotational disorder of the molecules in the columns.	19
Fig. 1.14	: Structure of the columnar helical phase.	19
Fig. 1.15	: Structure of the columnar lamellar phase.	20
Fig. 1.16	: Structure of the columnar tetragonal phase.	20
Fig. 1.17	: General structure of bent-core (banana-shaped) liquid crystals.	21
Fig. 1.18	: Schiff base-mercury mesogens.	23
Fig. 1.19	: Smectic ferrocenyl Schiff bases.	23
Fig. 1.20	: Dithiolene metallomesogen.	23
Fig. 1.21	: The archetypical metal–salicylaldimine systems.	24
Fig. 1.22	: Copper bis- β -diketonate metallomesogens.	25
Fig. 1.23	: Binuclear discogen based on the β -diketonates.	25
Fig. 1.24	: Metallomesogens based on diaminoaryl-bridged enamino-ketones.	26
Fig. 1.25	: Bis(salicylaldiminate) copper(II) complexes.	26

Fig. 1.26	: Mixed copper–lanthanide d-f metallomesogens.	27
CHAPTER 3	: BIDENTATE [N,O]-DONOR SALICYLALDIMINE SCHIFF BASE LIGAND AND ITS MESOMORPHIC AND PHOTOLUMINESCENT TETRAHEDRAL d¹⁰-METAL COMPLEXES	46-70
Fig. 3.1	: Platelet texture of [ZnL ₂] upon cooling at 127 °C.	51
Fig. 3.2	: DSC thermogram of [ZnL ₂].	51
Fig. 3.3	: Fibrous texture of [CdL ₂] upon cooling at 228 °C.	52
Fig. 3.4	: DSC thermogram of [CdL ₂].	52
Fig. 3.5	: PXRD pattern of [ZnL ₂] recorded at 122 °C (a) and (b) at 80 °C.	54
Fig. 3.6	: The ‘herringbone’ model for the self-assembled rod-like complex molecules in smectic E phase.	54
Fig. 3.7	: PXRD profile of [CdL ₂] at 210 °C.	56
Fig. 3.8	: UV-visible spectra of the ligand and complexes (CH ₂ Cl ₂ ; 10 ⁻⁵ M).	58
Fig. 3.9	: Photoluminescence spectrum of [CdL ₂] (10 ⁻⁵ M; λ _{ex.} = 325nm).	58
Fig. 3.10	: (a) Optimized structure of the ligand, HL.	62
	: (b) Optimized structure of [ZnL ₂].	62
	: (c) Optimized structure of [CdL ₂].	62
	: (d) Optimized structure of [HgL ₂].	63
CHAPTER 4	: TETRADENTATE [N₂O₂]-DONOR ASYMMETRIC ‘SALEN’ TYPE SCHIFF BASE LIGANDS AND THEIR MESOMORPHIC AND PHOTOLUMINESCENT ZINC(II) COMPLEXES	71-95
Fig. 4.1	: POM image of Zn-16dap upon cooling at 125°C.	78
Fig. 4.2	: DSC profile of (a) Zn-12dap, (b) Zn-14dap and (c) Zn-16dap.	78
Fig. 4.3	: PXRD pattern of Zn-16dap at (a) 100 °C and (b) at room temperature (30 °C).	80
Fig. 4.4	: Anti-parallel interdigitated organization of the molecules in lamello-columnar phase.	81
Fig. 4.5	: (a) UV-visible absorption spectra of the 16dap and Zn-16dap in chloroform (2×10 ⁻⁵ M) and (b) Intensity (normalized) vs. wavelength photoluminescence profile for Zn-16dap in chloroform solution (2×10 ⁻⁵ M), solid state and in mesophase (λ _{ex.} = 330nm).	83

Fig. 4.6	: UV-visible absorption spectra (a), fluorescence spectra ($\lambda_{\text{exc.}} = 330\text{nm}$; with 10% attenuator) (b) of Zn-16dap ($2 \times 10^{-5}\text{M}$) in different non-coordinating and coordinating solvents and (c) the 'H-type' dimer in solution of non-coordinating solvents.	85
Fig. 4.7	: Concentration dependence of UV-visible absorption spectra of Zn-16dap in CHCl_3 solutions.	86
Fig. 4.8	: DFT optimized structure of a representative complex, Zn-16dap.	89
Fig. 4.9	: Frontier molecular orbitals of Zn-16dap.	90
CHAPTER 5	: SYNTHESIS, MESOMORPHISM AND PHOTOPHYSICAL PROPERTIES OF TETRADENTATE $[\text{N}_2\text{O}_2]$-DONOR 'SALPHEN' TYPE SCHIFF BASE LIGANDS AND THEIR VO(IV), Ni(II), Cu(II) AND Zn(II) COMPLEXES	96-191
Fig. 5.1	: ^1H NMR spectrum of a representative ligand (16fpd).	117
Fig. 5.2	: Polarizing optical micrographs of (a) 16fpd at 29°C , (b) 16cpd at 30°C and (c) 16bpd at 50°C .	118
Fig. 5.3	: DSC traces (1 st heating) of 16fpd, 16cpd, and 16bpd.	118
Fig. 5.4	: DSC profiles (1 st cooling scan) of (a) 16fpd (b) 16cpd and (c) 16bpd.	119
Fig. 5.5	: One-dimensional intensity vs. 2θ profile of (a) 16fpd, (b) 16cpd and (c) 16bpd.	121
Fig. 5.6	: Absorption(left) and photoluminescence(right) spectra ($\lambda_{\text{exc.}} = 336\text{nm}$) of the ligands in dichloromethane solution ($1 \times 10^{-5}\text{M}$, r.t.)	123
Fig. 5.7	: Photoluminescence spectra of the ligands ($\lambda_{\text{exc.}} = 386\text{nm}$) in the solid state.	124
Fig. 5.8	: Photoluminescence spectra of the ligands ($\lambda_{\text{exc.}} = 386\text{nm}$) in the mesophase. Inset shows the PL image of 16cpd obtained on irradiation with a light of wavelength 366nm.	124
Fig. 5.9	: (a) Optimized electronic structure of 16fpd.	126
	(b) Optimized electronic structure of 16bpd.	126
Fig. 5.10	: Absorption spectra of oxovanadium(IV) complexes in dichloromethane solution ($1 \times 10^{-5}\text{M}$, r.t.).	128
Fig. 5.11	: Polarizing optical micrographs of (a) VO-16fpd at 188°C and (b) VO-16cpd at 221°C .	129
Fig. 5.12	: DSC profile of (a) VO-16fpd and (b) VO-16cpd.	130

Fig. 5.13	: (a) PXRD pattern of VO-16fpd at 200°C, (b) PXRD pattern of VO-16fpd at 100°C and (c) model for the molecular organization in the mesophase.	131
Fig. 5.14	: PXRD profile of VO-16cpd at (a) 240°C, (b) 100°C and (c) molecular organization in the mesophase.	132
Fig. 5.15	: Optimized electronic structure of a representative complex (VO-16cpd).	134
Fig. 5.16	¹ H NMR spectrum of a representative Ni(II) complex (Ni-16fpd).	136
Fig. 5.17	: Optical micrographs of (a) Ni-16fpd at 99°C, (b) Ni-16fpd at 25°C, (c) Ni-16cpd at 130°C, and (d) Ni-16bpd at 110°C.	137
Fig. 5.18	: DSC profile of (a) Ni-16fpd, (b) Ni-16cpd and (c) Ni-14bpd.	138
Fig. 5.19	: PXRD profile of Ni-16fpd at (a) 110°C and (b) at 80°C.	140
Fig. 5.20	: PXRD profile of Ni-16cpd at (a) 140°C and at (b) 50°C.	141
Fig. 5.21	: PXRD pattern for Ni-16bpd at 141°C.	142
Fig. 5.22	: Top-view of cross-section of a disc formed by (a) antiparallel interdigitated stacking of molecules, (b) face to face stacking of molecules and (c) packing of the semi-discoid molecules within the columns in the mesophase.	142
Fig. 5.23	: Absorption (left) and photoluminescence (right) spectra ($\lambda_{exc.} = 390\text{nm}$) of the Ni(II) complexes in dichloromethane solution (1×10^{-5} M, r.t.).	145
Fig. 5.24	: Absorption spectra of Cu(II) complexes in dichloromethane solution (1×10^{-5} M, r.t.).	146
Fig. 5.25	: ¹ H NMR spectrum of a representative Zn(II) complex (Zn-16fpd).	149
Fig. 5.26	: Polarizing optical micrographs of (a) Zn-16fpd at 208°C, (b) Zn-16cpd at 189°C and (c) Zn-16bpd at 212°C.	150
Fig. 5.27	: DSC profiles of (a) Zn-16fpd, (b) Zn-16cpd and (c) Zn-16bpd.	150
Fig. 5.28	: (a) One-dimensional intensity vs. 2θ profile of Zn-16fpd at 220°C and (b) model for molecular organization in the mesophase.	152
Fig. 5.29	: One-dimensional intensity vs. 2θ profile Zn-16cpd at 194°C and (b) dimeric association of the molecules in the mesophase.	153
Fig. 5.30	: (a) One-dimensional intensity vs. 2θ profile of Zn-16bpd at 230°C and (b) model for molecular organization in the mesophase.	154
Fig. 5.31	: Absorption (left) and normalized photoluminescence (right) spectra ($\lambda_{exc.} = 320\text{nm}$) of the Zn(II) complexes in dichloromethane solution (1×10^{-5} M, r.t.).	156

Fig. 5.32	: Photoluminescence spectra of the Zn(II) complexes ($\lambda_{exc.} = 320\text{nm}$) in the solid state.	157
Fig. 5.33	: Absorption(left) and emission(right) spectra of (a) Zn-16fpd, (b) Zn-16cpd and (c) Zn-16bpd in non-coordinating and coordinating solvents ($\lambda_{exc.} = 320\text{nm}$; 10^{-5} M, r.t).	159
Fig. 5.34	: Concentration dependence of UV-visible absorption spectra of (a) Zn-16fpd, (b) Zn-16cpd and (c) Zn-16bpd in dichloromethane solution.	160
Fig. 5.35	: (a) Optimized electronic structure of Zn-16fpd.	161
	: (b) Optimized electronic structure of Zn-16cpd.	162
	: (c) Optimized electronic structure of Zn-16bpd.	162
Fig. 5.36	: (a) HOMO diagram of Zn-16cpd.	163
	: (b) LUMO diagram of Zn-16cpd.	163
Fig. 5.37	: ^1H NMR spectra of (a) 16c2pd, (b) Ni-16c2pd and (c) Zn-16c2pd.	166
Fig. 5.38	: POM photographs of (a) Ni-16c2pd at 150°C and (b) Zn-16c2pd at 160°C , on cooling.	169
Fig. 5.39	: DSC profiles for (a) Ni-12c2pd (second scan), (b) Ni-14c2pd (second scan) and (c) Ni-16c2pd (first and second scan).	169
Fig. 5.40	: DSC profiles for (a) Zn-12c2pd (first scan), (b) Zn-14c2pd (first scan) and (c) Zn-16c2pd (first scan).	170
Fig. 5.41	: X-ray diffraction pattern of Ni-16c2pd at (a) 126°C , (b) 110°C and (c) 80°C .	171
Fig. 5.42	: X-ray diffraction pattern of Zn-16c2pd (a) at 140°C and (b) at room temperature (25°C).	173
Fig. 5.43	: Schematic illustration of (a) unit cell of a two dimensional columnar oblique lattice ($p1$), (b) unit cell of a two dimensional rectangular columnar $p2mm$ lattice and (c) model for dimeric association of the molecules and molecular organization in the mesophase.	173
Fig. 5.44	: UV-visible spectra of 16c2pd and corresponding metal complexes in dichloromethane solution (1×10^{-5} M, r.t.).	175
Fig. 5.45	: Absorption (left) and normalized fluorescence emission (right) spectra of 16c2pd in dichloromethane (1×10^{-5} M, r.t.) solution (—) and solid state (----). Side panels show the photoluminescence pictures of solution (top) and solid state (bottom) respectively, as seen after irradiation with a light of 366nm .	176

	Absorption (left) and normalized fluorescence emission (right)	
Fig. 5.46	: spectra of Zn-16c2pd in dichloromethane (1×10^{-5} M, r.t.) solution (—), solid state (----) and mesophase (····). Side panels show the photoluminescence pictures of solution(top), solid state(middle) and mesophase(bottom), respectively, as seen after irradiation with a light of 366nm.	177
Fig. 5.47	: Solvent dependent UV-visible spectra of VO-16c2pd (conc. 1×10^{-5} M).	178
Fig. 5.48	: Solvent dependent UV-visible spectra of Ni-16c2pd (conc. 1×10^{-5} M).	178
Fig. 5.49	: Solvent dependent UV-visible spectra of Cu-16c2pd (conc. 1×10^{-5} M).	179
Fig. 5.50	: (a) UV-visible (left) and fluorescence (right) spectra of Zn-16c2pd in non-coordinating and coordinating solvents (1×10^{-5} M), (b) concentration dependent absorption spectra of Zn-16c2pd (CH_2Cl_2 , r.t.).	180
Fig. 5.51	: Optimized electronic structure of Zn-16c2pd.	183

LIST OF TABLES

SL No.	TITLE	Page No.
CHAPTER 3	BIDENTATE [N,O]-DONOR SALICYLALDIMINE SCHIFF BASE LIGAND AND ITS MESOMORPHIC AND PHOTOLUMINESCENT TETRAHEDRAL d¹⁰-METAL COMPLEXES	46-70
Table 3.1	: Phase transition data of [ZnL ₂] and [CdL ₂].	52
Table 3.2	: PXRD data of [ZnL ₂] and [CdL ₂].	56
Table 3.3	: UV-visible and photoluminescence data of ligand and metal complexes.	59
Table 3.4	: Selected bond lengths (Å) and bond angles (°) for zinc(II), cadmium(II) and mercury(II) complexes evaluated at B3LYP level.	63
Table 3.5	: Natural atomic charges and natural electron configuration of selected atoms of the ligand and zinc(II), cadmium(II) and mercury(II) complexes evaluated at B3LYP level.	64
CHAPTER 4	TETRADENTATE [N₂O₂]-DONOR ASYMMETRIC ‘SALEN’ TYPE SCHIFF BASE LIGANDS AND THEIR MESOMORPHIC AND PHOTOLUMINESCENT ZINC(II) COMPLEXES	71-95
Table 4.1	: Thermodynamic data for the Zn-ndap (n = 12, 14, 16) complexes. Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH; kJ mol ⁻¹).	79
Table 4.2	: PXRD data of Zn-16dap.	81
Table 4.3	: UV-visible and photoluminescence spectral data of the ligands (in CHCl ₃) and Zn-ndap (n = 12, 14, 16) complexes in different solvents.	86
Table 4.4	: Selected bond lengths (Å) and bond angles (°) of Zn-16dap optimized at the B3LYP level.	89
Table 4.5	: The experimental absorption bands and the electronic transitions calculated with TD-DFT/B3LYP method of the Zn-16dap complex.	91

CHAPTER 5	SYNTHESIS, MESOMORPHISM AND PHOTOPHYSICAL PROPERTIES OF TETRADENTATE [N₂O₂]-DONOR 'SALPHEN' TYPE SCHIFF BASE LIGANDS AND THEIR VO(IV), Ni(II), Cu(II) AND Zn(II) COMPLEXES	96-191
Table 5.1	: Thermodynamic data for the ligands. Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH ; kJ mol ⁻¹).	119
Table 5.2	: X-ray diffraction data of the ligands.	121
Table 5.3	: The optical absorption and photoluminescence data of the ligands in dichloromethane solution and in the solid state at 298 K.	125
Table 5.4	: Selected bond lengths (Å) and angles (°) and other related parameters of the salphen ligands evaluated at B3LYP level.	126
Table 5.5	: The UV-visible spectral data of VO(IV) complexes in dichloromethane solution at 298K.	128
Table 5.6	: Thermal data for the VO-nfpd and VO-ncpd complexes (n =12, 14, 16). Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH ; J/g).	130
Table 5.7	: X-ray diffraction data of the VO(IV) complexes.	133
Table 5.8	: Selected bond lengths (Å) and angles (°) and other related parameters of VO-16cpd evaluated at BLYP level.	135
Table 5.9	: Thermodynamic data for the Ni(II) complexes. Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH ; J/g).	137
Table 5.10	: PXRD data of Ni (II) complexes.	143
Table 5.11	: The absorption and photoluminescence data of the Ni(II) complexes in dichloromethane solution(10 ⁻⁵ M) at 298 K.	145
Table 5.12	: Absorption data of Cu(II) complexes in dichloromethane solution (10 ⁻⁵ M) at 298K.	147
Table 5.13	: Thermal data of Cu(II) complexes.	148
Table 5.14	: Thermodynamic data for the Zn(II) complexes. Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH ; kJ mol ⁻¹).	151
Table 5.15	: X-ray diffraction data of the Zn(II) complexes.	155
Table 5.16	: The optical absorption and photoluminescence data of the Zn(II) complexes in different solvents and in the solid state at 298 K.	158

Table 5.17	:	Selected bond lengths (Å) and angles (°) and other related parameters of Zn(II) complexes evaluated at B3LYP(for Zn-16fpd and Zn-16bpd)/ BLYP(for Zn-16cpd) level.	164
Table 5.18	:	Thermodynamic data for the Ni(II) and Zn(II) complexes. Transition temperatures are given in °C, and the corresponding enthalpy changes are in parentheses (ΔH; J/g).	170
Table 5.19	:	X-ray diffraction data of Ni-16c2pd and Zn-16c2pd.	174
Table 5.20	:	Absorption data of the ligands (n = 12, 14, 16) and the corresponding metal complexes in various solvents, molar absorption coefficient(ε) in M ⁻¹ cm ⁻¹ and photoluminescence data of ligands and Zn(II) complexes in solution and the solid state at 298 K.	181
Table 5.21	:	The UV-visible spectral data of VO-16c2pd, Ni-16c2pd and Cu-16c2pd in different solvents at 298K.	182
Table 5.22	:	Selected bond lengths (Å) and bond angles (°) of Zn-16c2pd optimized at the B3LYP level.	183
Table 5.23	:	Mesomorphism and photoluminescence of salphen ligands and corresponding metal complexes with different 'salphen' spacer substituents.	186

ABBREVIATIONS

• NLO	:	Non-linear optics
• OLEDs	:	Organic light emitting diodes
• LC	:	Liquid crystal
• DFT	:	Density Functional Theory
• TD-DFT	:	Time dependent-Density Functional Theory
• FT-IR	:	Fourier transform-Infra red
• NMR	:	Nuclear magnetic resonance
• FAB	:	Fast atom bombardment
• EQY	:	Emission Quantum Yield
• d	:	Doublet
• dd	:	Doublet of doublets
• t	:	Triplet
• POM	:	Polarizing optical microscopy
• DSC	:	Differential scanning calorimetry
• I	:	Isotropic
• 1D, 2D, 3D	:	One-, two- and three-dimensional
• PL	:	Photoluminescence
• M	:	Molarity
• HOMO	:	Highest occupied molecular orbitals
• LUMO	:	Lowest un-occupied molecular orbitals
• AcOH	:	Acetic acid
• EtOH	:	Ethanol
• MeOH	:	Methanol
• THF	:	Tetrahydrofuran
• m	:	Multiplet
• DCM	:	Dichloromethane
• ppm	:	Parts per million