Table of Contents

Abbreviations ix-x

Chapter 1 Introduction 1-2

Chapter 2 Review of literature 3-71

2.1 Introduction 3

2.2 Basics of nonlinear optics 3

2.3 Types of NLO effects 5

2.3.1 Second harmonic generation (SHG) 5

2.3.2 Third harmonic generation (THG) 5

2.4 Measurement of NLO response 5

2.4.1 Kurtz-Perry powder technique 5

2.4.2 Electric field induced second harmonic generation (EFISH) 6

2.4.3 Hyper-Rayleigh scattering (HRS) 6

2.4.4 Third-harmonic generation (THG) 7

2.4.5 Degenerate four wave mixing (DFWM) 7

2.5 Materials for second order nonlinear optics 7

2.5.1 Design of NLO materials 9

2.5.1.1 Electronic aspects: The two-level method 9

2.5.1.2 Structural aspects of NLO materials 10

2.5.1.3 Donor, acceptor and π-bridging groups 11

2.6 NLO response of ferrocene derivatives 15

2.6.1 Ferrocene chromophores with organic acceptor units 15

2.6.2 Pyridyl and bipyridyl acceptors 24

2.6.3 Ferrocene chromophores with metal complex base acceptor units 32

2.6.3.1 Metal nitrosyl complexes 32

2.6.3.2 Metal carbonyls 38

2.6.3.3 Bipyridyl metal complexes 40

2.6.4 Heteroaromatic acceptors 45

2.6.5 Acceptors with imine linkage 52

2.6.6 Carboranes as acceptors 54

2.6.7 Carbocations as acceptor moieties 58
Chapter 3 Nonlinear optical response of ferrocene based donor–π–acceptor “push-pull” chromophores

3.1 Introduction 72
3.2 Design, synthesis and characterization of ferrocene based “push-pull” chromophores 73
3.3 Structure, linear, NLO properties and electrochemistry of Group A chromophores 89
  3.3.1 UV-visible absorption studies 89
  3.3.2 Electrochemistry 97
  3.3.3 Recording of first-order hyperpolarizability, \( \beta \) values 99
  3.3.4 Spectroelectrochemical studies 100
3.4 Structure, linear, NLO properties and electrochemistry of Group B chromophores 102
  3.4.1 Thermogravimetric analysis of the chromophores 102
  3.4.2 UV-visible absorption studies 104
  3.4.3 Electrochemistry 112
  3.4.4 Recording of first-order hyperpolarizability, \( \beta \) values 113
3.5 Structure, linear, NLO properties and electrochemistry of Group C chromophores 117
  3.5.1 Thermogravimetric analysis of the chromophores 117
  3.5.2 UV-visible absorption studies 118
  3.5.3 Electrochemistry 124
  3.5.4 Recording of first-order hyperpolarizability, \( \beta \), values 127
3.6 Structure-property relationship of chromophores of Groups A, B and C 129
  3.6.1 Single crystal structural analysis and correlation of NLO behaviour 131
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6.2</td>
<td>Structure and first-order hyperpolarizability correlations</td>
<td>134</td>
</tr>
<tr>
<td>3.6.3</td>
<td>Intrinsic hyperpolarizability, $\beta_{o}^{int}$</td>
<td>135</td>
</tr>
<tr>
<td>3.7</td>
<td>Conclusions</td>
<td>141</td>
</tr>
<tr>
<td>3.8</td>
<td>Experimental section</td>
<td>141</td>
</tr>
<tr>
<td>3.8.1</td>
<td>Materials and methods</td>
<td>141</td>
</tr>
<tr>
<td>3.8.2</td>
<td>General instrumentation</td>
<td>142</td>
</tr>
<tr>
<td>3.8.3</td>
<td>Computational methods</td>
<td>143</td>
</tr>
<tr>
<td>3.8.4</td>
<td>Crystallographic techniques</td>
<td>143</td>
</tr>
<tr>
<td>3.8.5</td>
<td>Hyper-Rayleigh scattering</td>
<td>144</td>
</tr>
<tr>
<td>3.9</td>
<td>Synthetic procedures for reagents, donors and acceptors used in the synthesis of ferrocene “push-pull” chromophores</td>
<td>144</td>
</tr>
<tr>
<td>3.10</td>
<td>Cartesian co-ordinates of chromophores</td>
<td>154</td>
</tr>
<tr>
<td>3.11</td>
<td>References</td>
<td>159</td>
</tr>
<tr>
<td>Chapter 4</td>
<td><strong>Cation recognition behaviour of ferrocene based “push-pull” chromophores</strong></td>
<td>165-228</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>165</td>
</tr>
<tr>
<td>4.2</td>
<td>Ferrocene based chemosensors signalling spectroscopic and/or redox changes upon cation recognition</td>
<td>166</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Imines as binding sub-unit</td>
<td>170</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Imidazoles as the binding sub-unit</td>
<td>172</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Quinoxalines as the binding sub-unit</td>
<td>174</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Triazoles as the binding sub-unit</td>
<td>177</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Pyrazoles as the binding sub-unit</td>
<td>178</td>
</tr>
<tr>
<td>4.2.6</td>
<td>Miscellaneous binding sites</td>
<td>178</td>
</tr>
<tr>
<td>4.3</td>
<td>Ferrocene based chemodosimeters that operate through specific chemical reaction leading to spectroscopic and/or redox changes</td>
<td>180</td>
</tr>
<tr>
<td>4.4</td>
<td>Ferrocene based chemosensor for Cu$^{2+}$ - A dual channel signalling system</td>
<td>181</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Design, synthesis and characterization of 2-[5,5-dimethyl-3-(ferrocen-1-yl-vinyl)-cyclohex-2-enylidene]malononitrile</td>
<td>183</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Absorption spectral studies and pH stability</td>
<td>184</td>
</tr>
<tr>
<td>4.4.3</td>
<td>Spectrophotometric behaviour of 2-[5,5-dimethyl-3-(ferrocen-1-yl-vinyl)-cyclohex-2-enylidene]malononitrile towards metal ions</td>
<td>187</td>
</tr>
</tbody>
</table>
4.4.4 Electrochemical changes during the detection of Cu$^{2+}$ by 2-[5,5-dimethyl-3-(ferrocen-1-yl-vinyl)-cyclohex-2-enylidene]malononitrile

4.4.5 Proposed mechanism for the sensing of Cu$^{2+}$

4.4.6 Sensing of Cu$^{2+}$ by using solid supported chemosensor

4.4.7 Conclusions

4.5 Ferrocene-imine-pyrene dyad: Spectroscopic evaluation as chemodosimeter and application in bioimaging

4.5.1 Synthesis and characterization of ferrocone-imine- pyrene dyad

4.5.2 Absorption spectrum and changes upon addition of metal ions

4.5.3 Emission spectrum and changes upon addition of metal ions

4.5.4 Proposed mechanism of sensing of Cr$^{3+}$ by ferrocene-imine-pyrene dyad

4.5.5 Application of chemodosimeter in the sensing of Cr$^{3+}$ in breast cancer cells

4.5.6 Conclusions

4.6 Experimental

4.6.1 General instrumentation

4.6.2 Bioimaging studies

4.6.2.1 Cytotoxicity assay

4.6.2.2 Cell imaging study

4.6.3 Computational details

4.6.4 Materials and methods

4.6.4.1 Preparation of Cu$^{2+}$ complex of the chemosensor

4.6.4.2 Synthesis of (1E)-N-(ferrocenemethylene)pyren-1-amine

4.6.4.3 Isolation of the hydrolytic products of the titration of (1E)-N-(ferrocenemethylene)pyren-1-amine with Cr$^{3+}$

4.7 Cartesian co-ordinates of the “push-pull” chromophores

4.8 References

Chapter 5 Summary

List of publications and presentations