# LIST OF FIGURE

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHAPTER ONE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>The outer membrane receptors FhuA and FecA. Structures of ferrichrome receptor FhuA in its (a) ligand-free and (b) ligand-loaded conformations. The structures of the ferric citrate receptor FecA in the (c) siderophore-free and (d) siderophore-bound conformations.</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>The chemical structures of the Porphyrin, Annulene, Fe-Heme complex, and Mg-Chlorophyll complex.</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic mechanism showing siderophore-mediated iron uptake and release through membrane receptor.</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>Structural of Desferal®, Desferrioxamine-B.</td>
<td>6</td>
</tr>
<tr>
<td>1.5</td>
<td>Molecular structures of some typical examples of naturally occurring siderophores.</td>
<td>10</td>
</tr>
<tr>
<td>1.6</td>
<td>The different types of bidentate chelating groups in siderophores.</td>
<td>11</td>
</tr>
<tr>
<td>1.7</td>
<td>Structures of representative example of hydroxamate, catecholate, HOPO and mixed type of synthetic chelators (a) Trendrox (b) Medrox (R=H, R’=H, R”=H) (c) HOPOBactin (d) Tren(Sox)2cams (X=SO₃), respectively</td>
<td>13</td>
</tr>
<tr>
<td>1.8</td>
<td>Artificial siderophore analogues designed to encapsulate metal ion in central cavity.</td>
<td>16</td>
</tr>
<tr>
<td>1.9</td>
<td>Molecular structure of enterobactin showing three distinct units: central unit (domain I), spacer (domain II) and metal binding unit.</td>
<td>16</td>
</tr>
<tr>
<td>1.10</td>
<td>General schematic diagram showing design of tripodal metal chelators</td>
<td>17</td>
</tr>
<tr>
<td>1.11</td>
<td>Energy minimized structures of proposed ligands (a) TAME5OX (b) TMOM5OX and (c) CYTOM5OX.</td>
<td>18</td>
</tr>
<tr>
<td><strong>CHAPTER TWO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>a) Chemical structure of naturally occurring siderophore. (b) Comparison of the chelating units of bipyridine, catecholate and 8-hydroxyquinolinate.</td>
<td>53</td>
</tr>
<tr>
<td>2.2</td>
<td>General formula of the (a) 5-(X-phenylazo)-8-hydroxyquinoline, (b) Fmoc-2Oxn-OH and Fmoc-(5Ph) 2Oxn-OH.</td>
<td>56</td>
</tr>
<tr>
<td>2.3</td>
<td>The structures of the 8-hydroxyquinoline derivatives with substitution at C-5 position, and their metal chelate complexes.</td>
<td>57</td>
</tr>
<tr>
<td>2.4</td>
<td>Chemical structures of fluorescent molecular sensors based on 8-hydroxyquinoline.</td>
<td>58</td>
</tr>
<tr>
<td>2.5</td>
<td>Structure of 2-pyridine-8-hydroxyquinoline and its ruthenium complex.</td>
<td>58</td>
</tr>
<tr>
<td>2.6</td>
<td>The double stranded helicates (a) schematic representation, (b) crystal structure of cu complex and (c) 2,2’-(1E,1’E)-(4,4’-methylenebis(4,1-phenylene)bis(azan-1-yl-1-ylidene)) bis(methan-1-yl-1-ylidene)diquinolin-8-ol.</td>
<td>60</td>
</tr>
<tr>
<td>2.7</td>
<td>Quinolinate-ether dipodal ligands which are used as for the recognition of alkali metals.</td>
<td>61</td>
</tr>
</tbody>
</table>
2.8 8-hydroxyquinoline-containing (a) crown ether conjugates, and (b) tetraazacrown ethers.
2.9 Tripodal ligands containing benzene as a central unit and 8-hydroxyquinoline as metal biding sites.
2.10 Tripodal ligands containing (a) tri(aminoethyl)amine “tren” as back bone, (b) C-pivotal atom as spacer and grafted with various polyoxyethylene (POE) chains, with 8-hydroxyquinoline sub-sites.
2.11 Tripodal ligands containing cyclic (a) trilactone (b) 1,4,7-triazacyclononane, as anchors with 8-hydroxyquinoline sub-sites.
2.12 Tetrapodal hydroxyquinoline ligands for the coordination of rare earth ions.

CHAPTER-THREE

3.1 Structures of Tripodal O-TRENOX, N-TRENOX (and their sulfonyl derivatives), Csox, Cox200, Cox750 and Cox2000.
3.2 X-ray Structures of [Fe(COX-200)] and of [Fe(O-TRENSOX)].
3.3 Structure of 5,5’-2-(((8-hydroxyquinolin-5-yl) methylamino) methyl)-2-methylpropane-1,3-diyl) bis(azanediy1) bis(methylene) diquinolin-8-ol (TAME5OX).
3.4 Infra-red (IR) spectrum of TAME5OX (a) experimental (ATR) (b) theoretical (calculated by B3LYP/6-31G*).
3.5 Correlation between the experimental and theoretical IR frequencies of TAME5OX.
3.6 $^1$HNMR spectrum of TAME5OX: (a) experimental (DMSO, 300 MHz), inset showing splitting of protons of aromatic part of ligand, and (b) calculated (applying DFT/B3LYP/6-31G* method).
3.7 $^{13}$C NMR spectrum of TAME5OX (DMSO, 300 MHz), insets showing chemical shifts due to aromatic carbons, and aliphatic carbons.
3.8 Correlation between the experimental and theoretical (a) $^1$HNMR, and (b) $^{13}$CNMR, data of TAME5OX.
3.9 MS(ES+) mass spectrum of TAME5OX.
3.10 Potentiometric titration curve of TAME5OX.
3.11 UV-vis absorption spectra of TAME5OX (1.0×10$^{-5}$M) as a function of pH.
3.12 Dependence of the fluorescence emission spectra of aqueous solution of TAME5OX (1.0 × 10$^{-3}$M) on the change of the pH value from acidic to basic range (1.97-10.95 pH), T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm) with an excitation wavelength of 385 nm
3.13 Species distribution curves of TAME5OX containing species, computed from the protonation constants given in Table 2. Calculated for [TAME5OX]$_{tot}$ = 1×10$^{-5}$ M, Solvent : H$_2$O, I = 0.1M (KCl), T = 25.0(2)°C.
3.14 Correlation between the experimental log K and calculated ∆Gº of TAME5OX.
3.15 pH-dependent electronic spectra (absorption) of the nine species as a function of molar absorptivity and wavelength (a) predicted from Hypspec using experimental data and (b) calculated through TD-DFT/B3LYP method by employing 6-31G* basis set, for the protonation and deprotonation of ground state geometrical optimized neutral species (LH$_1$) of TAME5OX.
3.16 Proposed photoinduced electron transfer (PET) and photoinduced proton transfer (PPT) mechanisms between N-pyridyl and -OH groups of 8-HQ moieties of TAME5OX in protonated quinolinium, neutral, and deprotonated quinolinate states.

3.17 Calculated CAM–B3LYP/6–31G* energy levels and surfaces of frontier molecular orbitals (MOs) of TAME5OX in protonated, neutral, and deprotonated states.

3.18 TD-camB3LYP simulated emission spectra of TAME5OX as a function of protonation and deprotonation of excited state geometrical optimized neutral species (LH₃) of by employing 6-31G* basis set

3.19 Infra-red (IR) spectrum of Fe(TAME5OX).

3.20 Correlation between the experimental and theoretical IR frequencies of M(TAME5OX); [M= Fe, Al and Cr].

3.21 MS(ES+) mass spectrum of Fe(TAME5OX).

3.22 Potentiometric titration curves: (i) 1×10⁻⁵M TAME5OX, (ii) [TAME5OX]/[Fe³⁺] = 1/1, 1×10⁻⁵M, (iii) [TAME5OX]/[Al³⁺] = 1/1, 5×10⁻⁵M, (iv) [TAME5OX]/[Cr³⁺] = 1/1, 1×10⁻⁵M. Solvent H₂O, I = 0.1M (KCl), T= 25(2)°C, and ‘a’ is the moles of base added per mole of M[TAME5OX] present. Symbols and solid lines represent the experimental and calculated data.

3.23 UV-vis absorption spectra of 1:1 solution of M³⁺ and TAME5OX (1/1, 1×10⁻⁵M) as a function of p[H]. For [TAME5OX]/[Fe³⁺] (a) p[H] = 1.97-7.54 (b) p[H] = 8.34-11.04; for [TAME5OX]/[Al³⁺] (a) p[H] = 1.94-7.42 (b) p[H] = 9.26-11.70; and for [TAME5OX]/[Cr³⁺] (a) p[H] = 1.89-7.98 (b) p[H] = 8.04-10.85. Solvent H₂O, I = 0.1M (KCl), T= 25(2)°C.

3.24 Dependence of the emission spectra of 1:1 aqueous solution of M³⁺;TAME5OX = (1.0 × 10⁻⁵M) on the change of the pH value from acidic to basic range, T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm). (a) for Fe³⁺/TAME5OX (1.89-11.23 pH), (b) for Al³⁺/TAME5OX (1.97-11.04 pH), and (c) for Cr³⁺/TAME5OX (1.94-11.70 pH), with an excitation wavelength of 385, 370 and 345 nm.

3.25 Correlation between the experimental log K and calculated ∆G⁰ (a) Fe(TAME5OX) and (b) Cr(TAME5OX).

3.26 Species distribution curves of (a) Fe(TAME5OX), (b) Al(TAME5OX) and (c) Cr(TAME5OX) containing species, computed from the formation constants given in Table. Calculated for [TAME5OX]ₗtot = [M³⁺]ₗtot = 1×10⁻⁵ M, Solvent : H₂O, I= 0.1M (KCl), T = 25.0(2)°C.

3.27 Plot of pM versus p[H] for TAME5OX, pM = -log [M³⁺], calculated for [M³⁺] = 10⁻⁵M and [L] = 10⁻⁵M. (a) p[Fe], (b) p[Al], and (c) p[Cr].

3.28 pH-dependent electronic spectra (absorption) of the different metal complexes as a function of molar absorptivity and wavelength (a) predicted from Hypspec using experimental data and (b) calculated through TD-DFT/B3LYP method by employing 6-31G* basis set, for Fe(TAME5OX), Al(TAME5OX) and Cr(TAME5OX).

3.29 The DFT/B3LYP optimized ground state geometries of (a) TAME5OX, (b) Fe[TAME5OX], (c) Al[TAME5OX] and (d) Cr[TAME5OX] from 6–31G* level of calculation.
Simulated TD-DFT spectra of neutral (ML, M = Fe, Al and Cr) complexes of TAME5OX as a function of 6-31G* basis set employed in (a) UV/vis absorption by B3LYP for excitation energy determination. (b) Emission by cam-B3LYP for first excited state geometries of complexes

Calculated (B3LYP/6-31G*) frontier orbitals for the metal complexes of TAME5OX (Metal = Fe, Al and Cr, respectively).

Quenching of the fluorescence emission spectrum of TAME5OX (1.0×10⁻⁵M) in water at pH 7.4, T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm), upon increasing concentration of (a) Fe³⁺ from 0→1.2 equivalent (λₐₑᵢₘᵩ = 385 nm) (b) Cr³⁺ from 0→1.4 equivalent (λₐₑᵢₘᵩ = 345 nm).

Evolution of the fluorescence emission spectrum (λₐₑᵢₘᵩ = 371 nm, excitation and emission slit widths of 2.5 nm) of TAME5OX (1.0×10⁻⁶M) upon increasing concentration of Al³⁺ in ethanol from 0→1.0 equivalent at pH 7.4, T = 25.0(3)°C.

Tetrapodal hydroxyquinoline ligands for the coordination of rare earth ions

Coordination scan plots for the ligand (TAME5OX) with the varied coordination number for Ln³⁺ complexes.

Potentiometric titration curves: (i) 5×10⁻⁵M TAME5OX, (ii) [TAME5OX]/[La³⁺] = 1/1, 5×10⁻⁵M (iii) [TAME5OX]/[Eu³⁺] = 1/1, 5×10⁻⁵M, (iv) [TAME5OX]/[Tb³⁺] = 1/1, 5×10⁻⁵M, and (v) [TAME5OX]/[Er³⁺] = 1/1, 5×10⁻⁵M., Solvent H₂O, I = 0.1M (KCl), T= 25(2)°C, and ‘a’ is the moles of base added per mole of Ln[TAME5OX] present. Symbols and solid lines represent the experimental and calculate data, respectively.

UV–vis absorption spectra of 1:1 solution of Ln³⁺ and TAME5OX as a function of p[H], [TAME5OX] = [Ln³⁺]₀ = 5×10⁻⁵M, Solvent: H₂O, I = 0.1M(KCl), T = 25.0(2)°C. For La[TAME5OX]: (a) p[H] = 1.94-7.49 (b) p[H] = 7.51-10.82; for Eu[TAME5OX]: (a) p[H] = 1.93-7.34 (b) p[H] = 7.49-10.88; and for Er[TAME5OX] (a) p[H] = 1.94-7.44; (b) p[H] = 7.51-10.65.

Dependence of the emission spectra of 1:1 aqueous solution of Ln:TAME5OX (5.0 × 10⁻⁵M) on the change of the pH value from acidic to basic range, T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm). (a) for La[TAME5OX] (1.94-10.23 pH), (b) for Er[TAME5OX] (1.94-10.65 pH), (c) for Eu[TAME5OX] (1.7-12.3 pH) and (d) for Tb[TAME5OX] (1.9-12.5 pH); with an excitation wavelength of 325 nm for La and Eu and 380 nm for Er and Tb

Correlation between the Experimental Log K and Calculated ∆G° of (a) La(TAME5OX), (b) Eu(TAME5OX) (c) Tb(TAME5OX), and Er(TAME5OX).

Sparkle/PM7 optimized ground state geometries in COSMO (water) of complexes (a) TAME5OX, showing preorganized three oxine units as readiness for metal complex formation (b) La[TAME5OX], (c) Er[TAME5OX], (d) Eu[TAME5OX] and (e) Tb[TAME5OX].

Species distribution curves of La[TAME5OX], Er[TAME5OX], La[TAME5OX] and Er[TAME5OX], respectively, containing species, computed from the formation constants given in Table. Calculated for [TAME5OX]₀ = [Ln³⁺]₀ = 10⁻⁵ M, Solvent : H₂O, I = 0.1M (KCl), T = 25.0(2)°C.
3.42 Plot of pLn versus p[H] for TAME5OX, pLn = -log ([Ln$^{3+}$]), calculated for [Ln$^{3+}$] = 10$^{-5}$M and [L] = 10$^{-5}$M, for (a) Ln= La$^{3+}$ and Er$^{3+}$ and (b) Ln= Eu$^{3+}$ and Tb$^{3+}$.

3.43 pH-dependent electronic spectra of the different species as a function of molar absorptivity and wavelength (a) predicted from Hypspec using experimental data and (b) calculated by applying semi-empirical sparkle PM7/ZINDOS methods for Ln[TAME5OX] (Ln= La, Eu, Tb and Er).

3.44 Calculated energy gaps and surfaces of frontier molecular orbitals for the ground state of Ln[TAME5OX] complexes of different protonated, neutral and hydroxo- species, respectively, from ZINDO/S-CIS method.

3.45 Emission spectra of complexes computed at the sparkle/PM7 optimized excited state geometries. In CIS-ZINDO/S computation of the spectra, the coordinating centre has been assumed to be a 3+ point charge. For La[TAME5OX], Er[TAME5OX], Eu[TAME5OX] and Tb[TAME5OX] species.

CHAPTER-FOUR

4.1 Structures of tripodal ligands based on oxygen functions in sapcers (a) reference ligand (b) target ligand.

4.2 Molecular structures of tripodal 8-hydroxyquinoline chelators containing (a) benzene (cyclic), (b) tris(ethylamine), tren (acyclic) frame-works.

4.3 IR spectra of TMOM5OX (a) experimental (ATR, cm$^{-1}$), and (b) theoretical, calculated by B3LYP/6311-G*.

4.4 ¹H NMR spectrum of TMOM5OX: (a) experimental (DMSO, 300 MHz) and (b) calculated (applying DFT/B3LYP/6311G* method).

4.5 ¹³C NMR spectrum of TMOM5OX (DMSO, 300 MHz).

4.6 Correlation between the experimental and calculated values of (a) ¹H NMR Chemical shifts (b) ¹³C NMR chemical shifts and (c) IR frequencies.

4.7 MS(ES+) mass spectrum of TMOM5OX.

4.8 Potentiometric titration curve of 5×10$^{-5}$M TMOM5OX, Solvent H$_2$O, I = 0.1M (KCl), T= 25(2)ºC, ‘a’ moles of base added per mole of TMOM5OX present. Symbols and solid line represent the experimental and calculated data.

4.9 UV-vis absorption spectra of TMOM5OX (5.0×10$^{-5}$M) as a function of pH: (a) pH = 1.7-6.8; (b) pH = 7.2-10.7; (c) pH =10.9-12.7. [TMOM5OX] =5×10$^{-5}$M. Solvent: H$_2$O, I = 0.1M (KCI), T = 25.0(2)/C

4.10 Species distribution curves of TMOM5OX, computed from the pKa values given in text. Calculated for [TMOM5OX]$_{tot}$ = 10$^{-3}$M, Solvent:H$_2$O, I = 0.1M (KCI), T = 25.0(2)/C.

4.11 The ground state optimized geometries of TMOM5OX from the TD-DFT/B3LYP/6–311G* calculation.

4.12 Simulated (a) TD-DFT/B3LYP UV–vis absorption (b) TD-camB3LYP simulated emission, spectra of TMOM5OX as a function of protonation and deprotonation of ground state geometrical optimized neutral species (LH$_3$) by employing 6311-G* basis set.

4.13 Dependence of the fluorescence emission spectra of aqueous solution of TMOM5OX under acidic (a), neutral (b) and basic (c) conditions, respectively, on the change of the pH value (1.0→12.7), T = 25.0(3)/C at the concentration of 5.0×10$^{-5}$M in aqueous medium with an excitation
4.14 Calculated CAM-B3LYP/6–311G* energy levels and surfaces of frontier molecular (HOMO–LUMO) orbitals for the first excited state of TMOM5OX in protonated, neutral and deprotonated states.

4.15 Schematic indicating the level of theory employed for each of the steps involved in photoexcitation and photorelaxation processes.

4.16 Infra-red (IR) spectrum of Fe(TMOM5OX)

4.17 Correlation between the experimental and theoretical IR frequencies of M(TMOM5OX); [M= Fe, Al and Cr].

4.18 MS(ES+) mass spectrum of Fe(TMOM5OX).

4.19 Potentiometric titration curves: (i) 5×10⁻⁵ M TMOM5OX, (ii) [TMOM5OX]/[Fe³⁺] = 1/1, 5×10⁻⁵ M, (iii) [TMOM5OX]/[Al³⁺] = 1/1, 5×10⁻⁵ M, (iv) [TMOM5OX]/[Cr³⁺] = 1/1, 5×10⁻⁵ M. Solvent H₂O, I = 0.1 M (KCl), T= 25(2) °C, ‘a’ moles of base added per mole of TMOM5OX present. Symbols and solid lines represent the experimental and calculated data.

4.20 UV-vis absorption spectra of 1:1 solution of Fe³⁺ and TMOM5OX as a function of pH: (a) pH = 1.7-7.2; (b) pH = 7.6-12.8; [TMOM5OX] = [Fe³⁺]tot =5×10⁻⁵ M. Solvent: H₂O, I = 0.1M (KCl), T = 25.0(2) °C.

4.21 Species distribution curves of (a) Fe(TMOM5OX), (b) Al(TMOM5OX) and (c) Cr(TMOM5OX) species, computed from the stability constants given in text. Calculated for [TMOM5OX]ₜot = [M³⁺]ₜot = 10⁻⁵ M, Solvent:H₂O, I = 0.1M (KCl), T = 25.0(2) °C.

4.22 UV–vis absorption spectra of TMOM5OX (2 ml, 10⁻⁵ M) with addition of increasing amounts of Fe³⁺ (10⁻⁵ M) (0→3 equivalent) in ethanolic medium, T = 25.0(2) °C, (a) at pH 7.4, (b) at pH 12.

4.23 UV–vis absorption spectra of TMOM5OX (2 ml, 10⁻⁵ M) with addition of increasing amounts of Fe³⁺ (10⁻⁵ M) (0→3 equivalent) in ethanolic medium, T = 25.0(2) °C, (a) at pH 7.4, (b) at pH 12.

4.24 (a) Stagnation of the fluorescence emission spectrum (excitation and emission slit widths of 4.5 nm) of TMOM5OX (2.0×10⁻⁶ M) upon increasing concentration of Fe³⁺ in ethanol from 0→3.2 equivalent (b) Evolution of the fluorescence emission spectrum (excitation and emission slit widths of 2.5 nm) of TMOM5OX (2.0×10⁻⁶ M) upon increasing concentration of Al³⁺ in ethanol from 0→2 equivalent, at λexc = 331 nm, pH 7.4 and T = 25.0(3) °C.

4.25 Growth of the fluorescence emission spectrum of TMOM5OX upon change in concentration from 1×10⁻⁶ M→5×10⁻⁴ M, at λexc = 331 nm and T = 25.0(3) °C.

4.26 The absorption (a), excitation (b) and emission (c) spectra of TMOM5OX (2 ml, 10⁻⁴ M) and M(TMOM5OX) in ethanol, T = 25.0(2) °C, λexc=331 nm, (λem = 432 nm ,excitation and emission slit widths of 4.5 nm for TMOM5OX and corresponding Fe³⁺ and Cr³⁺ complexes and λem = 525 nm ,excitation and emission slit widths of 2.5 nm for Al³⁺ complex).

4.27 The absorption (a), excitation (b) and emission (c) spectra of solid ferric complex of TMOM5OX. (a) in suspension of nujol, (b-c) solid compound by fluorescent probe, T = 25.0(2) °C, (λexc = 362 nm and λem = 440 nm) ,excitation and emission slit widths of 4.5 nm.
4.28 The ground state optimized geometries and frontier molecular orbitals (HOMO and LUMO) of TMOM5OX and iron complex from the TD-DFT/B3LYP/6311G* calculation.

4.29 Simulated TD-DFT/B3LYP UV–vis absorption spectrum of Fe(TMOM5OX) complex as a function of the 6311-G* basis set. Insets; UV-vis spectrum of Fe(TMOM5OX) (a) Solid complex in nujol and (b) 1:1 aqueous solution (10⁻³M).

4.30 Simulated TD-DFT/B3LYP UV–vis absorption spectrum of Al(TMOM5OX) and Cr(TMOM5OX) complexes as a function of the 6311-G* basis set.

4.31 Potentiometric titration curves: (i) 5×10⁻⁵M TMOM5OX, (ii) [TMOM5OX]/[La³⁺] = 1/1, 5×10⁻⁵M, (iii) [TMOM5OX]/[Eu³⁺] = 1/1, 5×10⁻⁵M, (iv) [TMOM5OX]/[Tb³⁺] = 1/1, 5×10⁻⁵M and (v) [TMOM5OX]/[Er³⁺] = 1/1, 5×10⁻⁵M. Solvent H₂O, I = 0.1M (KCl), T= 25(2) °C, and ‘a’ is the moles of base added per mole of Ln[TMOM5OX] present. Symbols and solid lines represent the experimental and calculated data.

4.32 UV–vis absorption spectra of 1:1 solution of Ln³⁺ and TMOM5OX as a function of p[H], [TMOM5OX] = [Ln³⁺]ₗ𝑜₅ = 5×10⁻⁵M, Solvent: H₂O, I = 0.1M(KCl), T = 25.0(2) °C. For La[TMOM5OX]: (a) p[H] = 1.79–7.2 (b) p[H] = 8.21–12.29; for Eu[TMOM5OX]: (a) p[H] = 1.68-6.8 (b) p[H] = 7.2-12.2; for Tb[TMOM5OX]: (a) p[H] = 1.7-7.9 (b) p[H] = 8.2-12.5; and for Er[TMOM5OX] (a) p[H] = 1.71-6.83; (b) p[H] = 6.85-12.54. Insets showing spectral peak around 210 nm–215 nm (at concentration = 5×10⁻⁶M).

4.33 Dependence of the emission spectra of 1:1 aqueous solution of Ln: TMOM5OX (5.0 × 10⁻³M) on the change of the pH value from acidic to basic range, T = 25.0(3) °C (excitation and emission slit widths of 5.0 nm). (a) for La[TMOM5OX] (1.81–12.3), (b) for Er[TMOM5OX] (1.84–12.67 pH) pH, (c) for Eu[TMOM5OX] (1.7-12.3 pH) and (d) for Tb[TMOM5OX] (1.9-12.5 pH); with an excitation wavelength of 335, 390, 332 and 393 nm for Eu, Tb, La and Er.

4.34 Correlation between the experimental log K and calculated ∆G° (a)Eu(TMOM5OX) (b) Tb (TMOM5OX), (c) La[TMOM5OX] (d) Er[TMOM5OX].

4.35 Sparkle/PM7 optimized ground state geometries in COSMO (water) of complexes (a) TMOM5OX, showing preorganized three oxine units as readiness for metal complex formation, (b) Eu(TMOM5OX), (c) Tb[TMOM5OX] (d) La[TMOM5OX], (e) Er[TMOM5OX] and (f) Er[TMOM5OX].

4.36 Species distribution curves of (a) La[TMOM5OX], (b) Er[TMOM5OX], (c) Eu[TMOM5OX] and (d) Tb[TMOM5OX] containing species, computed from the formation constants given in Table 1. Calculated for [TMOM5OX]ₗ₅ = [Ln(III)]ₗ = 10⁻⁵ M, Solvent: H₂O, I = 0.1M (KCl), T = 25.0(2) °C.

4.37 Plot of pLn versus p[H] for TMOM5OX, pLn = -log [Ln³⁺], calculated for [Ln³⁺] = 10⁻⁵M and [L] = 10⁻⁵M. (a) p[Eu] and p[Tb], (b) pLa and pEr.
4.38 pH-dependent electronic spectra of the different species as a function of molar absorptivity and wavelength (a) predicted from Hypspec using experimental data and (b) calculated by applying semi-empirical sparkle PM7/ZINDOS methods for Ln[TMOM5OX] (Ln= La, Eu, Tb and Er, respectively).

4.39 Calculated energy gaps and surfaces of frontier molecular orbitals for the ground state of Ln[TMOM5OX] complexes of different protonated, neutral and hydroxo- species, respectively, from ZINDO/S-CIS method.

4.40 Emission spectra of complexes computed at the sparkle/PM7 optimized excited state geometries. In CIS–ZINDO/S computation of the spectra, the coordinating centre has been assumed to be a 3+ point charge. (a) La[TMOM5OX], (b) Er[TMOM5OX], (c) Eu[TMOM5OX] and (d) Tb[TMOM5OX] species.

CHAPTER FIVE

5.1 Molecular structure of highly preorganized tripodal ligand (left) and its isomers of La-complex (right) showing bowl-shaped structure preorganized for uptake of metal ion

5.2 Molecular structure of tripodal ligands containing cyclic (a) trilactone (b) 1,4,7-triazacyclononane, as anchors with 8-hydroxyquinoline sub-sites

5.3 Infra-red (IR) spectrum of CYTOM5OX (a) experimental (ATR) (b) theoretical (calculated by B3LYP/6-31G*).

5.4 Correlation between the experimental and theoretical IR frequencies of CYTOM5OX.

5.5 $^1$H NMR spectrum of CYTOM5OX: (a) experimental (DMSO d$_6$, 300 MHz), inset showing splitting of protons of 8-hydroxyquinoline moiety, spacer and the signals of backbone, respectively part of ligand, and (b) calculated (applying DFT/B3LYP/6-31G*) method

5.6 $^{13}$C NMR spectrum of CYTOM5OX (DMSO, 300 MHz), inset showing chemical shifts due to aromatic carbons.

5.7 Correlation between the experimental and theoretical (a) $^1$H NMR, and (b) $^{13}$C NMR, data of CYTOM5OX

5.8 MS(ES+) mass spectrum of CYTOM5OX.

5.9 Potentiometric titration curve of CYTOM5OX (1×10^{-5}M). Solvent H$_2$O, I = 0.1M (KCl), T= 25(2)°C, and ‘a’ is the moles of base added per mole of CYTOM5OX present. Symbols and solid lines represent the experimental and calculated data

5.10 Potentiometric titration curve of CYTOM5OX (1×10^{-5}M). Solvent H$_2$O, I = 0.1M (KCl), T= 25(2)°C, and ‘a’ is the moles of base added per mole of CYTOM5OX present. Symbols and solid lines represent the experimental and calculated data

5.11 Distribution curves of CYTOM5OX ligand computed from the pKa values given in Table 2 at pH 2-12. Calculated for [CHTOM5OX]$_{tot}$ = 1×10^{-5} M, Solvent : H$_2$O, I = 0.1M (KCl), T = 25.0(2)°C.

5.12 Correlation between the experimental log K and calculated $\Delta G^\circ$ of CYTOM5OX

5.13 pH-dependent electronic spectra (absorption) of the six species as a function of molar absorptivity and wavelength (a) predicted from Hypspec
using experimental data and (b) calculated through TD-DFT/B3LYP method by employing 6-31G* basis set for the protonation and deprotonation of ground state geometrical optimized neutral species (LH₃) of CYTOM5OX.

5.14 (a) Energetically optimized structure by DFT/B3LYP and (b) drawing of molecular orbitals evaluated at TD-DFT, of the free ligand species LH₃ of CYTOM5OX.

5.15 TD-camB3LYP simulated emission spectra of CYTOM5OX as a function of protonation and deprotonation of excited state geometrical optimized neutral species (LH₃) of by employing 6-31G* basis set set.

5.16 Experimental infra-red (ATR) spectra of (a) Fe(CYTOM5OX), (b) Al(CYTOM5OX) and (c) Cr(CYTOM5OX).

5.17 Correlation between the experimental and theoretical IR frequencies of M(CYTOM5OX); [M= Fe, Al and Cr].

5.18 MS(ES+) mass spectra of (a) Fe(CYTOM5OX), (b) Al(CYTOM5OX) and (c) Cr(CYTOM5OX).

5.19 Potentiometric titration curves: (i) 1×10⁻⁵ M CYTOM5OX, (ii) [CYTOM5OX]/[Fe³⁺] = 1/1, 1×10⁻⁵ M, (iii) [CYTOM5OX]/[Al³⁺] = 1/1, 5×10⁻⁵ M, (iv) [CYTOM5OX]/[Cr³⁺] = 1/1, 1×10⁻⁵ M. Solvent H₂O, I = 0.1M (KCl), T= 25(2) °C, and ‘a’ is the moles of base added per mole of M[CYTOM5OX] present. Symbols and solid lines represent the experimental and calculated data, respectively.

5.20 UV-vis absorption spectra of 1:1 solution of M³⁺ and CYTOM5OX as a function of p[H]: (a) p[H] = 1.9-7.3 (b) p[H] = 7.5-10.2, for [CYTOM5OX]/[Fe³⁺] = 1/1; (c) p[H] = 1.8-7.4 (d) p[H] = 7.5-10.6, for [CYTOM5OX]/[Al³⁺] = 1/1; and (e) p[H] = 1.9-7.4 (f) p[H] = 7.5-10.6, for [CYTOM5OX]/[Cr³⁺] = 1/1; [CYTOM5OX] = [M³⁺]tot = 1×10⁻⁵ M, Solvent: H₂O, I = 0.1M(KCl), T = 25.0(2) °C.

5.21 Dependence of the emission spectra of 1:1 aqueous solution of M:CYTOM5OX (5.0 × 10⁻⁵ M) on the change of the pH value from acidic to basic range (~1.9-10.6), T = 25.0(3) °C (excitation and emission slit widths of 5.0 nm) (a) for Fe[CYTOM5OX], with an excitation wavelength of 350 nm, (b) for Al[CYTOM5OX] with an excitation wavelength of 325 nm, and (c) for Cr[CYTOM5OX], with an excitation wavelength of 335 nm.

5.22 Correlation between the experimental log K and calculated ∆Gº of (a) Fe(CYTOM5OX), (b) Cr(CYTOM5OX) and (c) Al(CYTOM5OX).

5.23 Species distribution curves of (a) Fe(CYTOM5OX), (b) Al(CYTOM5OX) and (c) Cr(CYTOM5OX) containing species, computed from the formation constants given in Table. Calculated for [CYTOM5OX]tot = [M³⁺]tot = 1×10⁻⁵ M, Solvent : H₂O, I = 0.1M (KCl), T = 25.0(2) °C.

5.24 Plot of pM versus p[H] for CYTOM5OX, pM = -log [M³⁺], calculated for [M³⁺] = 10⁻⁵ M and [L] = 10⁻⁵ M. (a) p[Al], (b) p[Cr], and (c) p[Fe].

5.25 pH-dependent electronic spectra (absorption) of the four species as a function of molar absorptivity and wavelength (a) predicted from Hypspec using experimental data and (b) calculated through TD-DFT/B3LYP method by employing 6-31G* basis set, for Fe(CYTOM5OX).

5.26 The DFT/B3LYP optimized ground state geometries of (a) Fe(CYTOM5OX), (b) Al(CYTOM5OX) and (c) Cr(CYTOM5OX) from
6−31G* level of calculation.

5.27 Simulated TD-DFT spectra of neutral (ML, M = Fe, Al and Cr) complexes of CYTOM5OX as a function of 6−31G* basis set employed in (a) UV/vis absorption by B3LYP for excitation energy determination; (b) Emission by cam-B3LYP for first excited state geometries of complexes.

5.28 Quenching of the fluorescence emission spectrum of CYTOM5OX (1.0×10−5M) in water at pH 7.4, T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm), upon increasing concentration of (a) Fe3+ from 0→1.2 equivalent (λexc = 390 nm) (b) Cr3+ 0→1.5 equivalent (λexc = 395 nm).

5.29 Evolution of the fluorescence emission spectrum (lexc = 325 nm, excitation and emission slit widths of 2.5 nm) of CYTOM5OX (1.0×10−6 M) upon increasing concentration of Al3+ in ethanol from 0→2.0 equivalent at pH 7.4, T = 25.0(3)°C.

5.30 Potentiometric titration curves: (i) 5×10−5M CYTOM5OX, (ii) [CYTOM5OX]/[La3+] = 1/1, 5×10−5M (iii) [CYTOM5OX]/[Eu3+] = 1/1, 5×10−5M, (iv) [CYTOM5OX]/[Tb3+] = 1/1, 5×10−5M, and (v) [CYTOM5OX]/[Er3+] = 1/1, 5×10−5M. Solvent H2O, I = 0.1M (KCl), T = 25(2) °C, and ‘a’ is the moles of base added per mole of Ln[CYTOM5OX] present. Symbols and solid lines represent the experimental and calculate data

5.31 UV−vis absorption spectra of 1:1 solution of Ln3+ and CYTOM5OX as a function of pH: (a) p[H] = 1.8−7.4 (b) p[H] = 7.6−10. 2, for [CYTOM5OX]/[Eu3+] = 1/1; (c) p[H] = 1.81−7.4 (d) p[H] = 7.5−10.2 for [CYTOM5OX]/[Tb3+] = 1/1; and (a) p[H] = 1.87−7.4 (b) p[H] = 7.56−10.27, for [CYTOM5OX]/[Er3+] = 1/1; [CYTOM5OX] = [Ln3+] = 5×10−5M, Solvent: H2O, I = 0.1M(KCl), T= 25(2) C.

5.32 Dependence of the emission spectra of 1:1 aqueous solution of Ln: CYTOM5OX (5.0 × 10−5M) on the change of the pH value from acidic to basic range, T = 25.0(3)°C (excitation and emission slit widths of 5.0 nm), with an excitation wavelength of 390 nm for each system (a) for La[CYTOM5OX], (1.88−10.20 pH), (a) for Eu[CYTOM5OX], (1.88−10.13 pH) and (b) for Tb[CYTOM5OX] (1.87−10.27 pH). (a) for Eu[CYTOM5OX], (1.83−10.18 pH).

5.33 Plot of pLn versus p[H] for CYTOM5OX, pLn = -log [Ln3+], calculated for [Ln3+] = 10−5M and [L] = 10−5M, for Ln= La3+, Eu3+, Tb3+ and Er3+

5.34 Species distribution curves of (a) La[CYTOM5OX], (b) Eu[CYTOM5OX], (c) Tb[CYTOM5OX], and (d) Er[CYTOM5OX] containing species, computed from the formation constants given in Table. Calculated for [CYTOM5OX] = [Ln3+] = 10−5 M, Solvent : H2O, I = 0.1M(KCl), T = 25.0(2) C.

5.35 Correlation between the experimental log K and calculated ∆Gº of (a) La(CYTOM5OX), (b) Eu(CYTOM5OX), (c) Tb(CYTOM5OX) and (d) Er(CYTOM5OX).

5.36 Sparkle/PM7 optimized ground state geometries of complexes: (a) La(CYTOM5OX), (b) Eu(CYTOM5OX), (c) Tb(CYTOM5OX) and (d) Er(CYTOM5OX)

5.37 Simulated CIS-ZNDO/s absorption spectra of neutral (LnL, Ln = La, Eu, Tb and Er) complexes of CYTOM5OX for ground state geometries of complexes