CHAPTER IV
RESULTS AND DISCUSSION

4. 9,10-PHENANTHRENEQUINONE(PQ)-L-PHENYLALANINE(Phe) SYSTEM

This chapter deals with synthesis, characterization, magnetic, electrochemical, thermal and BSA binding studies of Schiff base derived from 9,10-phenanthrenequinone and L-Phenylalanine (PQ-Phe) and its mononuclear Mn(III) and Fe(III) complexes.

4.1 PQ-Phe Schiff base ligand

4.1.1 Elemental Analysis

The Schiff base ligand PQ-Phe was synthesized by the condensation of 9,10-phenanthrenequinone and L-Phenylalanine, and its Mn(III) and Fe(III) complexes were also synthesized. The ligand and its complexes are found to be stable in air and soluble in common organic solvents like DMSO, DMF etc. The elemental analytical data of the Schiff base ligand and its complexes are given in the Table 4.1.1. The values obtained are comparable with the theoretical values.

Table 4.1.1 Elemental analytical data of PQ-Phe Schiff base ligand and its complexes
(Theoretical values in parentheses)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Formula</th>
<th>% M</th>
<th>% C</th>
<th>% N</th>
<th>% H</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQ-Phe</td>
<td>C_{32}H_{26}N_{2}O_{4}</td>
<td>-</td>
<td>(76.5)</td>
<td>(5.6)</td>
<td>(5.2)</td>
</tr>
<tr>
<td>Mn(III)-PQ-Phe</td>
<td>[Mn(C_{32}H_{26}N_{2}O_{6})]OAc</td>
<td>9.14</td>
<td>66.31</td>
<td>4.67</td>
<td>4.29</td>
</tr>
<tr>
<td>Fe(III)-PQ-Phe</td>
<td>[Fe(C_{32}H_{26}N_{2}O_{6})]Cl</td>
<td>9.36</td>
<td>63.96</td>
<td>4.79</td>
<td>4.16</td>
</tr>
</tbody>
</table>
4.1.2 $^{13}$C-NMR spectral analysis

The $^{13}$C-NMR spectrum of the Schiff base ligand (PQ-Phe) is shown in Fig 4.1.2.

$^{13}$C-NMR Spectrum of PQ-Phe shows signals in the range $\delta$ 123.98-139.98 which are due to aromatic carbons. The Signal at $\delta$ 163.04 corresponds to the two azomethine carbons. Signal at $\delta$ 180.32 is due to the two carboxylate carbon atoms.

Fig 4.1.2 $^{13}$C-NMR Spectrum of PQ-Phe
4.1.3 EI mass spectral analysis

The EI mass spectrum of PQ-Phe, given in Fig 4.1.3, shows the molecular ion (M⁺) peak at m/z = 502 corresponding to the molecular weight of the ligand. The peaks at m/z = 472, 293, 250, 234, 207, 179, 151, 104 and 75 corresponds to various fragments C_{32}H_{26}N_{2}O_{4}, C_{18}H_{16}N_{2}O_{2}, C_{16}H_{13}NO_{2}, C_{16}H_{13}NO, C_{14}H_{18}N_{2}, C_{10}H_{9}NO_{2}, C_{9}H_{9}O_{2}, C_{8}H_{8} and C_{6}H_{5} respectively. This confirms the structure of PQ-Phe.

Fig 4.1.3 EI Mass Spectrum of PQ-Phe
4.1.4 FT-IR Spectral Studies

The FT-IR spectrum of PQ-Phe Schiff base ligand is illustrated in Fig 4.1.4. The spectrum shows a significant intense peak at 1673 cm\(^{-1}\) due to the imine \(\nu(-\text{C}=\text{N})\) vibration. The intense peak at 1589 cm\(^{-1}\) is due to \((\text{COO}^-)\) asymmetric stretching and the peak at 1417 cm\(^{-1}\) is due to \((\text{COO}^-)\) symmetric stretching vibration of carboxylic acid group. This confirms the successful condensation of 9,10-phenanthrenequinone and L-phenylalanine, forming the Schiff base PQ-Phe.

![FT-IR Spectrum of PQ-Phe](image)

*Fig 4.1.4 FT-IR Spectrum of PQ-Phe*
4.1.5 Structure of Schiff base ligand PQ-Phe

From the above analytical and spectral data, the Schiff base PQ-Phe, has been confirmed to be a potentially tetradentate ligand. This established structure, given in Fig.4.5.1, was drawn using ChemBioOffice 12.0 software, and simulated for minimum energy. The low energy indicates stability of the ligand.

In brief

Colour: Yellow  
Yield: 60%  
Melting point: 158 °C  
Mol Formula: C_{32}H_{26}N_{2}O_{4}  
% of Elements: C, 75.98; H, 5.53; N, 5.25  
^{13}\text{C NMR: } \delta 163.04 (C=N), \delta 180.32 (COO^-)  
EI Mass: m/z =502  
FT-IR: 1673 cm^{-1}(C=N), 1589 cm^{-1}(COO^-)  

Total energy: 32.131 k cal/mol

Fig 4.1.5 Structure of PQ-Phe
4.2 Mn(III)-PQ-Phe Schiff base Complex

4.2.1 Vibrational Spectral Studies

The FT-IR spectra of Mn(III)-PQ-Phe is shown in Fig 4.2.1. It exhibits the imino (C=N) stretching frequency at 1642 cm\(^{-1}\). This vibration band has been shifted to lower frequency, compared to that of the free ligand (1673 cm\(^{-1}\)). This indicates the coordination of imino nitrogen atoms to Mn(III) ion.\(^1\) Further, the absorption band due to the asymmetric stretching vibrations of COO\(^-\) group has been shifted from 1589 cm\(^{-1}\) to 1576 cm\(^{-1}\), and the symmetrical stretching band is shifted from 1417 cm\(^{-1}\) to 1409 cm\(^{-1}\), confirming the bonding of the Mn(III) ion by the carboxylato oxygen atom. The broad band at 3439 cm\(^{-1}\) is due to intermolecular hydrogen bonding of –OH stretching resulting from water molecule. The new bands observed at 532 cm\(^{-1}\) and 438 cm\(^{-1}\) corresponding respectively to Mn-O and Mn-N stretching vibrations, also demonstrate the coordination of the imino nitrogen and carboxylato oxygen atoms to Mn(III) ion. The remaining two positions of the octahedron will be occupied by two water molecules.

![Fig 4.2.1 FT-IR Spectrum of Mn(III)-PQ-Phe complex](image)
4.2.2 Electronic Spectral Studies

The electronic spectrum of Mn(III)-PQ-Phe complex is illustrated in Fig 4.2.2a and 4.2.2b. The UV-Vis spectrum shows three transition bands. The high intense band at 350 nm is due to ligand field absorptions. Instead appearance of two less intense bands around 610 nm and 730 nm correspond to $^5B_{1g} \rightarrow ^5E_g$ and $^5B_{1g} \rightarrow ^5B_{2g}$ transitions respectively. This implies that the complex has undergone tetragonal distortion from regular octahedral geometry.[2]

Fig 4.2.2a Electronic spectra of Mn(III)-PQ-Phe complex

Fig 4.2.2b Electronic spectra of Mn(III)-PQ-Phe complex in wavelength range 500-800 nm
4.2.3 Molar conductance value

The molar conductance of the Mn(III)-PQ-Phe complex in DMF (Table 4.2.3), was found to be 50.24 Smol\(^{-1}\)cm\(^2\) at 27\(^\circ\)C. This value of molar conductance suggests that the complex is 1:1 electrolyte.\(^{[3]}\) The Mn(III) ion is coordinated by two imino nitrogen atoms, two carboxylato oxygen atoms, and two water molecules. Hence the effective charge of the complex will be +1, and one acetate ion will be present outside the coordination sphere of the complex.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance (S mol(^{-1})cm(^2))</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(III)-PQ-Phe</td>
<td>50.24</td>
<td>1:1 electrolyte</td>
</tr>
</tbody>
</table>

4.2.4 Magnetic moment measurement

The magnetic moment value of the complex Mn(III)-PQ-Phe, as given in Table 4.2.4, is 4.96 B.M\(^{[2]}\), which corresponds to the presence of four unpaired electrons in the complex. This means the Mn(III)-PQ-Phe is spin free complex, with all the four electrons unpaired during complexation. Hence, an octahedral geometry can be assigned to the complex with outer orbital sp\(^3\)d\(^2\) configuration.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic moment, (\mu_{\text{eff}}) (B.M)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(III)-PQ-Phe</td>
<td>4.96</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>
4.2.5 Electrochemical studies

The electrochemical behavior of the Mn(III)-PQ-Phe complex has been studied by cyclic voltammetry (CV) in DMF medium at a scan rate of 0.1 V/s. The cyclic voltammogram of the complex is depicted in Fig 4.2.5, shows one irreversible cathodic wave in the potential range $E_{pc} = -0.15$ V which can be attributed to the Mn(III)/Mn(II) couple. The presence of larger electronegative oxygen in oxyimine moiety decreases the electron density around the Mn(III) ion and eases reduction processes at low negative potential.$^{[4,5]}$

![Cyclic voltammogram of Mn(III)-PQ-Phe complex](image)
4.2.6 Thermal Studies

The thermal analysis of Mn(III)-PQ-Phe complex (Fig 4.2.6) was investigated by thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). The sample was heated at 1 atm pressure with a heating rate of 10 °C min⁻¹ and a temperature range of 20–700 °C. The TGA curve of the Mn(III)-PQ-Phe indicates that the thermal decomposition occurs at three steps. The first degradation step takes place in the range of 110-185 °C with a weight loss of 5.6% which may be assigned to the removal of two coordinated water molecules. The second decomposition step occurs at 220-325 °C accompanied by the weight loss of 35.4% owing to the loss of free acetate ion and carbonyl moiety. The third degradation step occurs at 330-540 °C, with a weight loss of 50% assigned to the removal of phenylalanine moiety. Above 540 °C metal oxides are present. Thus, the TGA and DTG provide the useful information about the coordination of water molecules to the metal ion and the stability of the complexes.

Fig 4.2.6 TG-DTG curves of Mn(III)-PQ-Phe complex
4.2.7 Structure of Mn(III)-PQ-Phe Complex

The observations from the analytical and spectral data discussed above clearly indicate that the Schiff base ligand PQ-Phe coordinate the Mn(III) ion through two imino nitrogen atoms and two carboxylato oxygen atoms, leading to an octahedral geometry for the complex. The remaining two positions are occupied by water molecules. Mn(III)-PQ-Phe is an outer orbital complex with \( sp^3d^2 \) configuration. The structure elucidated for the complex is drawn using ChemBioOffice 12.0 software and simulated for minimum energy and is given in Fig 4.2.7. The low energy of 133.537 k.cal/mol, signify stability of the complex.

**In brief**

Colour: Brown
Yield: 52%
Mol Formula: \([\text{Mn(C}_{32}\text{H}_{28}\text{N}_{2}\text{O}_{4})]\text{OAc}\)
% of Elements: Mn, 9.14; C, 66.31;
H, 4.29; N, 4.67
IR: 1642, 1576, 1409, 532, 438 cm\(^{-1}\)
UV: 610, 730 nm
\( \Lambda_M \): 50.24 S mol\(^{-1}\)cm\(^2\)
\( \mu \): 4.96 BM

Total energy: 133.537 kcal/mol

**Fig 4.2.7 Structure of Mn(III)-PQ-Phe complex**
4.3 Fe(III)-PQ-Phe Schiff base Complex

4.3.1 Vibrational Spectral Studies

The FT-IR spectra of Fe(III)-PQ-Phe is given in Fig 4.3.1. The spectrum exhibits the imino (C=N) stretching frequency at 1648 cm$^{-1}$. This imino frequency band has been shifted to lower frequency, compared to that of the free ligand (1673 cm$^{-1}$). This indicates the coordination of imino nitrogen atoms to Fe(III) ion.[1] Moreover, the absorption band for asymmetric stretching vibrations of COO$^-$ group has been shifted from 1589 cm$^{-1}$ to 1572 cm$^{-1}$, and symmetric stretching band is shifted from 1417 cm$^{-1}$ to 1402 cm$^{-1}$, confirming the bonding of the Fe(III) ion by the carboxylato oxygen atom. The broad band at 3439 cm$^{-1}$ is due to intermolecular hydrogen bonding of –OH stretching resulting from water molecules present inside the coordination sphere of the complex. The FT-IR spectrum of Fe(III)-PQ-Phe complex also exhibits additional bands at 530 and 457 cm$^{-1}$, corresponding respectively to $\nu$(Fe-O) and $\nu$(Fe-N) stretching vibrations.

![Fig 4.3.1 FT-IR Spectrum of Fe(III)-PQ-Phe complex](image)
4.3.2 Electronic Spectral Studies

The electronic spectra of Fe(III)-PQ-Phe complex is depicted in Fig 4.3.2a as well as 4.3.2b. This spectra show three bands at 750 nm, 600 nm and 325 nm. These bands can be assigned respectively to $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow ^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow ^4E_g$ transitions of the Fe(III) ion in the octahedral environment. Hence, octahedral geometry can be allocated to the Fe(III)-PQ-Phe complex.[6]

![Fig 4.3.2a Electronic spectra of Fe(III)-PQ-Phe complex](image1)

![Fig 4.3.2b Electronic spectra of Fe(III)-PQ-Phe complex in wavelength range 500-800 nm](image2)
4.3.3 Molar conductance value

The molar conductance of the Fe(III)-PQ-Phe complex in DMF (Table 4.3.3), was found to be 52.14 Smol⁻¹cm² value at 27°C. This value of molar conductance suggests that the complex is 1:1 electrolyte. The Fe(III) ion is coordinated by two imino nitrogen atoms, two carboxylato oxygen atoms, and two water molecules. Hence the effective charge of the complex will be +1, and one chloride ion will be present outside the coordination sphere of the complex. This is in agreement with the molar conductance values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance (S mol⁻¹cm²)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)-PQ-Phe</td>
<td>52.14</td>
<td>1:1 electrolyte</td>
</tr>
</tbody>
</table>

4.3.4 Magnetic moment measurement

The magnetic moment value of the complex Fe(III)-PQ-Phe, as given in Table 4.3.4, is 5.82² B.M, which corresponds to the presence of five unpaired electrons in the complex. This means the Fe(III)-PQ-Phe is spin free complex, with all the five electrons in the d⁵ Fe(III) ion are not paired during complexation. Hence, an octahedral geometry can be assigned to the complex with outer orbital sp³d² configuration.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic moment, µ_eff (B.M)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)-PQ-Phe</td>
<td>5.82</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>
4.3.5 EPR Spectral Studies

The liquid nitrogen temperature (LNT) solid state X-band EPR spectrum of the Fe(III)-PQ-Phe complex is shown in Fig 4.3.5. The spectrum exhibits six hyperfine lines, indicating the presence of five free electrons in the complex system. This observation agrees well with the result obtained from magnetic moment studies. The spectrum exhibits $g_{av} = 2.0$, which can be attributed to the iron in the distorted octahedral site symmetry.\cite{7,8}
4.3.6 Electrochemical studies

The electrochemical behavior of the Fe(III)-PQ-Phe complex has been studied by cyclic voltammetry (CV) in acetonitrile medium at a scan rate of 0.1 V/s. The cyclic voltammogram of the complex is depicted in Fig 4.3.6 which shows three cathodic waves in the potential range $E_{pc}^1 = -0.3$ V, $E_{pc}^2 = -0.91$ V and $E_{pc}^3 = -1.29$ V. The first irreversible cathodic process can be attributed to the Fe(III)/Fe(II) couple. The second irreversible cathodic process can be assigned to the Fe(II)/Fe(I) couple. It has been observed that the cyclic voltammogram of the ligands features an irreversible reduction at about -1.0 V. The more negative (ca. -1.3 V) cathodic process in the complex is close to that observed for the ligand.\cite{9} The less reduction potentials of the Fe(III) ion are due to presence of larger electronegative oxygen in oxyimine moiety, which decreases the electron density around the Fe(III) ion and eases reduction processes at low negative potentials.\cite{4,5}

![Fig 4.3.6 Cyclic voltammogram of Fe(III)-PQ-Phe complex](image-url)
4.3.7 Thermal Studies

The thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG) of Fe(III)-PQ-Phe complex was investigated by heating the sample at 1 atm pressure with a heating rate of 10 °C min⁻¹ and a temperature range of 20–700 °C. The thermogram of the complex is given in Fig 4.3.7. The TGA curve of the complex exhibits three thermal decomposition steps. The first degradation occurs in the range of 150-180 °C with 5.7% weight loss which is assigned to the removal of two coordinated water molecules. The second decomposition step occurs at 180-380 °C accompanied by the weight loss of 32.3% which is assigned to the loss of free chloride ion and carbonyl moiety. The third degradation step occurs at 400-525 °C, with a weight loss of 51% assigned to the removal of phenylalanine moiety. Above 525 °C metal oxides exist.

Fig 4.3.7 TG-DTG curves of Fe(III)-PQ-Phe complex
4.3.8 Structure of Fe(III)-PQ-Phe Complex

The analytical and spectral data discussed in this section clearly confirm that the Schiff base ligand PQ-Phe coordinate the Fe(III) ion through two imino nitrogen atoms and two carboxylato oxygen atoms, leading to an octahedral geometry for the complex. The remaining two positions are occupied by water molecules. Fe(III)-PQ-Phe is an outer orbital complex with sp³d³ configuration. The structure elucidated for the complex is drawn using ChemBioOffice 12.0 and simulated for minimum energy. It is given in Figure 4.3.8. The low energy (141.413 kcal/mol) indicate the stability of the complex.

In brief

Colour: Green
Yield: 65%
Mol Formula: [Fe(C₃₂H₂₈N₂O₄)]Cl
% of Elements: Fe, 9.36; C, 63.96; H, 4.16; N, 4.79
IR: 1648, 1572, 1402, 530, 457 cm⁻¹
UV: 750, 600, 325 nm
λₘ: 52.14 S mol⁻¹ cm²
μ: 5.82 BM
EPR: gᵥ = 2.0, 6 lines

Total energy: 141.413 kcal/mol

Fig 4.3.8 Structure of Fe(III)-PQ-Phe
4.4 BSA binding studies of Mn(III)/Fe(III)-PQ-Phe complexes

4.4.1 Fluorescence spectroscopy

The fluorescence intensity of BSA was quenched around 350 nm on addition of increasing concentration of the metal complexes but the emission maximum did not move to shorter or longer wavelength. BSA contains three fluorophores namely, tryptophan, tyrosine and phenylalanine. The intrinsic fluorescence of BSA is mainly due to tryptophan alone, because phenylalanine has a very low quantum yield and the fluorescence of tyrosine is almost totally quenched if it is ionized or near an amino group, a carbonyl group, or a tryptophan residue.\cite{10}

The decrease in fluorescence intensity of BSA on addition of metal complexes is due to the interaction of the metal complexes with BSA. The effect of the metal complexes on BSA is shown in Fig 4.4.1a and 4.4.1b. The quenching of BSA may be either dynamic or static. Dynamic quenching is caused due to collision. Static quenching occurs as a result of complex formation between BSA and the metal complexes. The quenching mechanism of metal complexes with BSA was probed by Stern-Volmer equation. The $K_{sv}$ values obtained from the linear plot of $F_0/F$ vs. $[Q]$ are furnished in Table 4.4.1. The inset in Fig 4.4.1a and 4.4.1b corresponds to the Stern-Volmer plot. The fluorescence lifetime of BSA in the absence of quencher ($\tau_0$) is $10^{-8}$ s.\cite{11} The bimolecular quenching rate constant $K_q (= K_{sv}/\tau_0)$ calculated is provided in Table 4.4.1.
Fig 4.4.1a Emission spectra of BSA at varying concentration of Mn(III)-PQ-Phe (T=298 K and λ=280 nm), c(BSA)= 2.0 x 10^{-6} molL^{-1}, c(Mn(III)-PQ-Phe) = 2, 4, 6, 8, 10 x 10^{-6} molL^{-1}.

Fig 4.4.1b Emission spectra of BSA at varying concentration of Fe(III)-PQ-Phe (T=298 K and λ=280 nm), c(BSA)= 2.0 x 10^{-6} molL^{-1}, c(Fe(III)-PQ-Phe) = 2, 4, 6, 8, 10 x 10^{-6} molL^{-1}.
Table 4.4.1 $K_{sv}$ and $K_q$ values of Mn(III) and Fe(III)-PQ-Phe complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$K_{sv}$ (x $10^4$ Lmol$^{-1}$)</th>
<th>$K_q$ (x $10^{12}$ Lmol$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(III)-PQ-Phe</td>
<td>5.33</td>
<td>5.33</td>
</tr>
<tr>
<td>Fe(III)-PQ-Phe</td>
<td>5.49</td>
<td>5.49</td>
</tr>
</tbody>
</table>

According to literature\cite{12} for dynamic quenching, the maximum scatter collision quenching constant of various quenchers with the biopolymer is $2.0 \times 10^{10}$ Lmol$^{-1}$s$^{-1}$. The obtained values of $K_q$ are greater than $2.0 \times 10^{10}$ Lmol$^{-1}$s$^{-1}$ indicating that the quenching of BSA by the metal complexes is not dynamic.
4.4.2 Absorption spectroscopy

Therefore, the quenching mechanism arises due to static quenching i.e., due to formation of complex between BSA and metal complexes. This was further confirmed by absorption spectra of BSA and BSA-metal complex solutions (Fig 4.4.2a. and 4.4.2b). The absorption wavelength of BSA at 285 nm shifted slightly to the right on addition of solution of metal complexes indicating the complex formation between BSA and metal complexes.

Fig 4.4.2a UV-Vis absorption spectra of BSA and BSA-Mn(III)-PQ-Phe solutions:
\[ c(\text{BSA}) = c(\text{Mn(III)}-\text{PQ-Phe}) = 2 \times 10^{-6} \text{molL}^{-1}. \]

Fig 4.4.2b UV-Vis absorption spectra of BSA and BSA-Fe(III)-PQ-Phe solutions:
\[ c(\text{BSA}) = c(\text{Fe(III)}-\text{PQ-Phe}) = 2 \times 10^{-6} \text{molL}^{-1}. \]
4.4.3 Analysis of binding constants and binding sites and binding energy

The linear fitting plots of log\((F_0 - F)/F\) vs. log\([Q]\) (Fig 4.4.3a. and 4.4.3b) gives the values of binding constants and binding sites which are furnished in Table 4.4.3.

Fig 4.4.3a Double-log plot of Mn(III)-PQ-Phe quenching effect on BSA fluorescence at 298K

Fig 4.4.3b Double-log plot of Fe(III)-PQ-Phe quenching effect on BSA fluorescence at 298K
Table 4.4.3 Binding constant, Binding site and Binding energy values of Mn(III)/Fe(III)-PQ-Phe complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Binding constant (x 10^4 Lmol^-1)</th>
<th>Binding site</th>
<th>Binding energy(ΔG) KJmol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(III)-PQ-Phe</td>
<td>4.67</td>
<td>0.98</td>
<td>-26.64</td>
</tr>
<tr>
<td>Fe(III)-PQ-Phe</td>
<td>4.18</td>
<td>0.88</td>
<td>-26.36</td>
</tr>
</tbody>
</table>

These results suggest that there is a strong binding force between the BSA and the metal complexes. There is a hydrophobic cavity in BSA which is favorable for the hydrophobic metal complexes to enter into BSA and interacts with it. The number of binding sites for both the complexes is approximated to 1 which suggests that there is only one binding site on the protein. The negative ΔG values (Table 4.4.3) indicate the spontaneity of BSA-metal complexes binding.
4.5 Molecular docking studies of Mn(III)/Fe(III)-PQ-Phe complexes

Molecular docking technique is used to understand the ligand-protein interaction which can substantiate our experimental results. The best energy ranked results revealed that the complexes Mn(III)-PQ-Phe and Fe(III)-PQ-Phe are located within sub-domain IIA hydrophobic cavity, and this is clearly illustrated in Fig 4.5.1 and 4.5.2 respectively for Mn(III) and Fe(III)-PQ-Phe complexes.

Fig 4.5.1 Molecular docked model of Mn(III)-PQ-Phe located within sub-domain IIA

Fig 4.5.2 Molecular docked model of Fe(III)-PQ-Phe located within sub-domain IIA