CHAPTER VI
RESULTS AND DISCUSSION

6. 9,10-PHENANTHRENEQUINONE(PQ)-L-TYROSINE(Tyr) SYSTEM

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

6.1 PQ-Tyr Schiff base ligand

6.1.1 Elemental Analysis

The Schiff base ligand PQ-Tyr was synthesized by the condensation of 9,10-phenanthrenequinone and L-Tyrosine, and was complexed with Mn(III) and Fe(III) metal ions. The ligand and its complexes are stable in air, and soluble in common organic solvents like DMF, DMSO etc. The elemental analytical data of the Schiff base ligand and its complexes are given in the Table 6.1.1. It is found that the experimental values agree well with the calculated values.

Table 6.1.1 Elemental analytical data of PQ-Tyr 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-Tyr</td>
<td>C_{32}H_{26}N_{2}O_{6}</td>
<td>-</td>
<td>70.79</td>
<td>5.36</td>
<td>4.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(71.9)</td>
<td>(5.2)</td>
<td>(4.9)</td>
</tr>
<tr>
<td>Mn(III)-PQ-Tyr</td>
<td>[Mn(C_{32}H_{28}N_{2}O_{8})]OAc</td>
<td>8.53</td>
<td>60.92</td>
<td>4.79</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.8)</td>
<td>(61.6)</td>
<td>(4.9)</td>
</tr>
<tr>
<td>Fe(III)-PQ-Tyr</td>
<td>[Fe(C_{32}H_{28}N_{2}O_{8})]Cl</td>
<td>8.79</td>
<td>61.54</td>
<td>4.47</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.9)</td>
<td>(61.5)</td>
<td>(4.5)</td>
</tr>
</tbody>
</table>

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6.1.2 $^{13}$C-NMR spectral analysis

The $^{13}$C-NMR spectrum of the Schiff base ligand (PQ-Tyr) is shown in Fig 6.1.2.

$^{13}$C-NMR Spectrum of PQ-Tyr shows signals in the range $\delta$ 114.12-136.16 which are due to aromatic carbons. The signal at $\delta$ 155.98 is assigned to two -OH attached carbons. The Signal at $\delta$ 163.19 corresponds to the two azomethine carbons. Signal at $\delta$ 180.47 is due to the two carboxylate carbons.

![Fig 6.1.2 $^{13}$C-NMR Spectrum of PQ-Tyr](image)
6.1.3 EI mass spectral analysis

The EI mass spectrum (Fig 6.1.3) of PQ-Tyr shows the molecular ion ($M^+$) peak at m/z = 534 corresponding to the molecular weight of the ligand. The peaks at m/z = 485, 440, 383, 305, 253, 236, 204, 181, 154, 136, 108, 78 and 58 corresponds to various fragments $C_{31}H_{23}N_2O_4$, $C_{26}H_{20}N_2O_5$, $C_{20}H_{18}N_2O_6$, $C_{18}H_{13}N_2O_3$, $C_{16}H_{13}NO_2$, $C_{13}H_9NO_2$, $C_{14}H_8N_2$, $C_{12}H_9NO$, $C_{12}H_10$, $C_7H_6NO_2$, $C_7H_5O$, $C_6H_4$ and $C_2H_2O_2$ respectively. This confirms the structure of PQ-Tyr.

![Fig 6.1.3 EI Mass Spectrum of PQ-Tyr](image-url)
6.1.4 FT-IR Spectral Studies

The FT-IR spectra (Fig 6.1.4) of PQ-Tyr Schiff base ligand shows an intense peak at 1673 cm\(^{-1}\) due to the imine \(\nu(-C=N)\) vibration. The peaks due to (COO\(^{-}\)) asymmetric stretching and (COO\(^{-}\)) symmetric stretching vibration of carboxylic acid group are observed in the regions of 1589 cm\(^{-1}\) and 1450 cm\(^{-1}\) respectively. The band at 3205 cm\(^{-1}\) corresponds to \(\nu(-OH)\) stretching vibration. This confirms the successful condensation of 9,10-Phenanthrenequinone and L-Tyrosine.

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

Fig 6.1.4 FT-IR Spectrum of PQ-Tyr
6.1.5 Structure of Schiff base ligand PQ-Tyr

From the above analytical and spectral data, the Schiff base PQ-Tyr, has been confirmed to be a potentially tetradentate chelator. The ChemDraw structure of the ligand is illustrated in Fig 6.1.5. The energy of the molecule is only 42.032 kcal/mol, signifying the stability of the ligand.

**In brief**

- Colour: Yellow
- Yield: 80%
- Melting point: 178 °C
- Mol Formula: $C_{32}H_{26}N_2O_6$
- % of Elements: C, 70.79%; H, 4.79%; N, 5.36
- $^{13}$C NMR: $\delta$ 163.19 (C=N), $\delta$ 180.47 (COO$^-$)
- El Mass: m/z =534
- FT-IR: 1673 cm$^{-1}$(C=N), 1589 cm$^{-1}$(COO$^-$)

Total energy: 42.032 kcal/mol

**Fig 6.1.5 Structure of PQ-Tyr**
6.2 Mn(III)-PQ-Tyr Schiff base Complex

6.2.1 Vibrational Spectral Studies

The FT-IR spectra of Mn(III)-PQ-Tyr is shown in Fig 6.2.1. The imino (C=N) stretching frequency at 1598 cm\(^{-1}\) in this spectrum has been shifted to lower frequency when compared to that of the free ligand (1673 cm\(^{-1}\)). This explains the coordination of imino nitrogen atoms to Mn(III) ion.\(^{[1]}\) Further, there exists a shifting of absorption band due to asymmetric stretching vibrations of COO\(^-\) group from 1589 cm\(^{-1}\) to 1512 cm\(^{-1}\), and the symmetrical stretching band is shifted from 1450 cm\(^{-1}\) to 1435 cm\(^{-1}\). This confirms the bonding of the carboxylato oxygen atoms to Mn(III) ion. The broad band at 3423 cm\(^{-1}\) is due to –OH stretching. The appearance of new bands at 547 cm\(^{-1}\) and 423 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.

![Fig 6.2.1 FT-IR Spectrum of Mn(III)-PQ-Tyr complex](image)
6.2.2 Electronic Spectral Studies

The electronic spectrum of Mn(III)-PQ-Tyr complex is illustrated in Fig 6.2.2a and 6.2.2b. It showed an intense and sharp charge transfer band at 280 nm and two spin allowed d-d transition bands at 530 nm and 720 nm which are characteristic of $^5\text{B}_{1g}\rightarrow^5\text{E}_g$ and $^5\text{B}_{1g}\rightarrow^5\text{B}_{2g}$ transitions respectively. These less intense and broad d-d transitions refer to the tetragonally distorted octahedral geometry of the complex.\textsuperscript{[2]}

![Fig 6.2.2a Electronic spectra of Mn(III)-PQ-Tyr complex](image)

**Fig 6.2.2a** Electronic spectra of Mn(III)-PQ-Tyr complex

![Fig 6.2.2b Electronic spectra of Mn(III)-PQ-Tyr complex in wavelength range 500-800 nm](image)

**Fig 6.2.2b** Electronic spectra of Mn(III)-PQ-Tyr complex in wavelength range 500-800 nm
6.2.3 Molar conductance value

The molar conductance value of the Mn(III)-PQ-Tyr complex in DMF (Table 6.2.3), was found to be 51.78 Smol$^{-1}$cm$^{2}$ at 27°C which 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 making the effective charge of the complex to be +1, which is neutralized by one acetate ion 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-Tyr</td>
<td>51.78</td>
<td>1:1 electrolyte</td>
</tr>
</tbody>
</table>

6.2.4 Magnetic moment measurement

The magnetic moment value of the complex Mn(III)-PQ-Tyr, as given in Table 6.2.4, is 4.89 B.M$^{[2]}$. This value explains the presence of four unpaired electrons in the complex which means that the Mn(III)-PQ-Tyr complex is spin free. 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-Tyr</td>
<td>4.89</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>
6.2.5 Electrochemical studies

The cyclic voltammogram of the Mn(III)-PQ-Tyr complex has been recorded in DMF medium at a scan rate of 0.1 V/s to study its redox property. The cyclic voltammogram of the complex is given in Fig 6.2.5. It exhibits two cathodic peaks in the potential range $E_{pc}^1 = -0.05$ V and $E_{pc}^2 = -1.4$ V and an anodic peak at $E_{pa} = 1.0$ V. The first and second cathodic peaks are irreversible in nature. The first cathodic peak is assigned to the formation of Mn(III)/Mn(II) couple. The second more negative cathodic peak may be assigned to the reduction of ligand.[9] The irreversible oxidation response is due to the oxidation of Mn(III) to Mn(IV). The electron donating group (–OH) as the mesomeric effect ability of the substituent on the phenyl ring of the Schiff base favored oxidation of Mn(III) to Mn(IV).[15]

![Cyclic voltammogram of Mn(III)-PQ-Tyr complex](attachment:image)
6.2.6 Thermal Studies

The TG-DTG curves of Mn(III)-PQ-Tyr complex (Fig 6.2.6) was obtained by heating the sample within a temperature range of 20–700 °C at heating rate of 10 °C min⁻¹ at 1 atm pressure. In Mn(III)-PQ-Tyr complex, the first step weight loss of 5.2% occurs at 150-180 °C. This loss in weight may be assigned to the removal of two coordinated water molecules which proves the presence of two water molecules inside the coordination sphere. The second step with a mass loss of 31.8% that exhibits in the temperature range of 220-290 °C refers to the loss of carbonyl moiety and free acetate ion. The removal of tyrosine moiety was observed in the temperature range of 300-440 °C with a weight loss of 51%. Above this temperature there exist metal oxides.
6.2.7 Structure of Mn(III)-PQ-Tyr Complex

Form the analytical and spectral data discussed above, it can be clearly concluded that the Schiff base ligand PQ-Tyr coordinates 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. The elucidated structure (Fig.6.2.7), exhibit low energy of 117.362 kcal/mol, which is obtained from ChemBioOffice 12.0 software. This clearly indicates the stability of the complex.

In brief

Colour: Brown
Yield: 57%
Mol Formula: [Mn(C_{32}H_{26}N_{2}O_{6})]OAc
% of Elements: Mn, 8.53; C, 60.92; H, 4.63; N, 4.79
IR: 1598, 1512, 1435, 547, 423 cm\(^{-1}\)
UV: 720, 530, 280 nm
\(\Lambda_M\): 51.78 S mol\(^{-1}\)cm\(^2\)
\(\mu\): 4.89 BM

Total energy: 117.362 kcal/mol

Fig 6.2.7 Structure of Mn(III)-PQ-Tyr
6.3 Fe(III)-PQ-Tyr Schiff base Complex

6.3.1 Vibrational Spectral Studies

The FT-IR spectra of Fe(III)-PQ-Tyr is shown in Fig 6.3.1. The imino (C=N) stretching frequency at 1611 cm\(^{-1}\) in this spectrum has been shifted to lower frequency when compared to that of the free ligand (1673 cm\(^{-1}\)). This explains the coordination of imino nitrogen atoms to Fe(III) ion.\(^{[1]}\) Further, there exists a shifting of absorption band due to asymmetric stretching vibrations of COO\(^-\) group from 1589 cm\(^{-1}\) to 1513 cm\(^{-1}\), and the symmetrical stretching band is shifted from 1450 cm\(^{-1}\) to 1402 cm\(^{-1}\). This confirms the bonding of the carboxylato oxygen atoms to Fe(III) ion. The broad band at 3200 cm\(^{-1}\) is due to –OH stretching. The appearance of new bands at 528 cm\(^{-1}\) and 435 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 Fe(III) ion.

![FT-IR Spectrum of Fe(III)-PQ-Tyr complex](image.png)

Fig 6.2.1 FT-IR Spectrum of Fe(III)-PQ-Tyr complex
6.3.2 Electronic Spectral Studies

The electronic spectra of Fe(III)-PQ-Tyr complex is depicted in Fig 6.3.2a and 6.3.2b. It shows three bands at 670 nm, 525 nm and 275 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. These indicate the octahedral orientation of donor centre around Fe(III) ion.\textsuperscript{[6]}

![Fig 6.3.2a Electronic spectra of Fe(III)-PQ-Tyr complex](image1)

![Fig 6.3.2b Electronic spectra of Fe(III)-PQ-Tyr complex in wavelength range 500-800 nm](image2)
6.3.3 Molar conductance value

The molar conductance of the Fe(III)-PQ-Tyr complex in DMF is given in Table 6.3.3. The value of molar conductance 51.56 S mol$^{-1}$ cm$^2$ suggests the 1:1 electrolytic nature of the complex.$^{[3]}$ The Fe(III) ion being coordinated by two imino nitrogen atoms, two carboxylato oxygen atoms, and two water molecules, the effective charge of the complex will be +1, and one chloride ion will be present outside the coordination sphere of the complex agreeing to be 1:1 electrolyte.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance (S mol$^{-1}$ cm$^2$)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)-PQ-Tyr</td>
<td>51.56</td>
<td>1:1 electrolyte</td>
</tr>
</tbody>
</table>

6.3.4 Magnetic moment measurement

The magnetic moment value of the complex Fe(III)-PQ-Tyr (Table 6.3.4), is 5.93$^{[2]}$ B.M, which shows the presence of five unpaired electrons in the complex. This explains that the Fe(III)-PQ-Tyr is spin free complex, containing five unpaired electrons in the d$^5$ orbital of Fe(III) ion. Hence, the hybridization is sp$^3$d$^2$ leading to an octahedral geometry.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic moment, $\mu_{\text{eff}}$ (B.M)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)-PQ-Tyr</td>
<td>5.93</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>
6.3.5 EPR Spectral Studies

The solid state X-band EPR spectrum of the Fe(III)-PQ-Tyr complex in liquid nitrogen temperature (LNT) is depicted in Fig 6.3.5. The spectrum exhibits six hyperfine lines, indicating the presence of five unpaired electrons in the complex system which agrees well with the magnetic moment value. The $g_{av}= 2.14$ corresponds to the distorted octahedral geometry for the Fe(III)-PQ-Tyr complex.\[7,8\]
6.3.6 Electrochemical studies

The cyclic voltammogram of the Fe(III)-PQ-Tyr complex has been recorded in acetonitrile medium at a scan rate of 0.1 V/s to study its redox property. The cyclic voltammogram of the complex is given in Fig 6.3.6. It exhibits three cathodic peaks in the potential range $E_{pc}^1 = 0.57$ V, $E_{pc}^2 = -0.32$ V and $E_{pc}^3 = -0.89$ V and an anodic peak at $E_{pa} = 0.09$ V. The first and second cathodic peaks are irreversible in nature and assigned to the formation of Fe(III)/Fe(II) and Fe(II)/Fe(I) couples respectively. The third more negative cathodic peak (ca. -1.3 V) in the complex may be assigned to the reduction of free ligand. The irreversible oxidation response is due to the oxidation of Fe(III) to Fe(IV). The electron donating group (–OH) as the mesomeric effect ability of the substituent on the phenyl ring of the Schiff base favored oxidation of Fe(III) to Fe(IV).
6.3.7 Thermal Studies

The TG-DTG curves of Fe(III)-PQ-Tyr complex (Fig 6.3.7) was obtained by heating the sample within a temperature range of 20–700 °C at heating rate of 10 °C min⁻¹ at 1 atm pressure. In Fe(III)-PQ-Tyr complex, the first step weight loss of 5.5% occurs at 130-190 °C. This loss in weight may be assigned to the removal of two coordinated water molecules which proves the presence of two water molecules inside the coordination sphere. The second step with a mass loss of 31.5% that exhibits in the temperature range of 240-320 °C refers to the loss of free chloride ion and carbonyl moiety. The removal of tyrosine moiety was observed in the temperature range of 330-475 °C with a weight loss of 51%. Above this temperature there exist metal oxides.

Fig 6.3.7 TG-DTG curves of Fe(III)-PQ-Tyr complex
6.3.8 Structure of Fe(III)-PQ-Tyr Complex

The analytical and spectral data discussed above clearly confirm that the Schiff base ligand PQ-Tyr coordinate the Fe(III) ion through two imino nitrogen atoms and two carboxylato oxygen atoms, forming an octahedral geometry. The remaining two positions of the octahedron are occupied by two water molecules. The structure elucidated for Fe(III)-PQ-Tyr is simulated for minimum energy using ChemBioOffice 12.0 software. The energy of the molecule is only 128.642 kcal/mol, signifying the stability of the complex. The structure is given in Figure 6.3.8.

In brief

Colour : Green
Yield: 68%
Mol Formula: \([\text{Fe(C}_3\text{H}_2\text{O}_6\text{N}_2\text{O}_6])\text{Cl}\]
% of Elements: Fe, 8.79; C, 61.54; H, 4.63; N, 4.47
IR: 1611, 1513, 1402, 528, 435 cm\(^{-1}\)
UV: 670, 525, 275 nm
\(\Lambda_M\): 51.56 S mol\(^{-1}\)cm\(^2\)
\(\mu\): 5.93 BM
EPR: \(g_{av} = 2.14\), 6 lines

Total energy: 128.642 kcal/mol

Fig 6.3.8 Structure of Fe(III)-PQ-Tyr
6.4 BSA binding studies of Mn(III)/Fe(III)-PQ-Tyr complexes

6.4.1 Fluorescence spectroscopy

Fluorescence quenching is the decrease of the quantum yield of fluorescence from a fluorophore induced by a variety of molecular interactions with quencher molecule. Fluorescence quenching can be dynamic, resulting from collisional encounters between the fluorophore and the quencher; or static, resulting from the formation of a ground state complex between the fluorophore and quencher.\cite{16} In both cases, molecular contact is required between the fluorophore and quencher for the fluorescence to occur. The dynamic and static quenching can be distinguished by Stern-Volmer equation.

The interaction of Mn(III)/Fe(III)-PQ-Tyr metal complexes with BSA are depicted in Fig 6.4.1a and 6.4.1b respectively. These figures show that with the addition of varying concentration of metal complex solutions, the fluorescence intensity of BSA around 350 nm decreased regularly and there was almost no shift of the emission wavelength. These phenomena indicated that the metal complexes could interact with BSA and quench its intrinsic fluorescence. The inset in Fig 6.4.1a and 6.4.1b shows the Stern-Volmer plot of $F_0/F$ vs. $[Q]$. The $K_{sv}$ values obtained are given in Table 6.4.1. The fluorescence lifetime of BSA in the absence of quencher ($\tau_0$) is $10^{-8}$ s.\cite{11} The bimolecular quenching rate constant of the biological macromolecule, $K_q (= K_{sv}/ \tau_0)$ is calculated and provided in Table 6.4.1.
Fig 6.4.1a Emission spectra of BSA in the presence of various concentration of Mn(III)-PQ-Tyr (T=298 K and λ=280 nm), c(BSA) = 2.0 x 10^{-6} \text{ molL}^{-1}, c(\text{Mn(III)-PQ-Tyr}) = 2, 4, 6, 8, 10 \times 10^{-6} \text{ molL}^{-1}.

Fig 6.4.1b Emission spectra of BSA in the presence of various concentration of Fe(III)-PQ-Tyr (T=298 K and λ=280 nm), c(BSA) = 2.0 x 10^{-6} \text{ molL}^{-1}, c(\text{Fe(III)-PQ-Tyr}) = 2, 4, 6, 8, 10 \times 10^{-6} \text{ molL}^{-1}.
Table 6.4.1 $K_{sv}$ and $K_q$ values of Mn(III) and Fe(III)-PQ-Tyr 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-Tyr</td>
<td>6.63</td>
<td>6.63</td>
</tr>
<tr>
<td>Fe(III)-PQ-Tyr</td>
<td>6.55</td>
<td>6.55</td>
</tr>
</tbody>
</table>

For dynamic quenching, the maximum scatter collision quenching constant of various quenchers with the biopolymer is 2.0 x 10$^{10}$ Lmol$^{-1}$s$^{-1}$.[12] The obtained values of $K_q$ are greater than 2.0 x 10$^{10}$ Lmol$^{-1}$s$^{-1}$, which indicated that the probable quenching mechanism of BSA-metal complex interaction was initiated by complex formation rather than by dynamic collision.
6.4.2 Absorption spectroscopy

In order to confirm the ground state complex formation between the protein and the quencher, UV-vis absorption spectra of BSA in the presence and absence of metal complexes were taken (Fig 6.4.2a. and 6.4.2b). It was found that absorption spectrum of BSA increased after the addition of metal complex solution, along with a red shift. This result confirmed that the quenching of BSA by the metal complexes was static quenching owing to complex formation.

**Fig 6.4.2a UV-vis absorption spectra of BSA and BSA-Mn(III)-PQ-Tyr solutions:**
\[ c(\text{BSA}) = c(\text{Mn(III)-PQ-Tyr}) = 2 \times 10^{-6} \text{ molL}^{-1}. \]

**Fig 6.4.2b UV-vis absorption spectra of BSA and BSA-Fe(III)-PQ-Tyr solutions:**
\[ c(\text{BSA}) = c(\text{Fe(III)-PQ-Tyr}) = 2 \times 10^{-6} \text{ molL}^{-1}. \]
6.4.3 Analysis of binding constants and binding sites and binding energy

The binding constant and binding site values which are obtained from linear fitting plots of \( \log \left[ \frac{(F_0-F)}{F} \right] \) vs. \( \log [Q] \) (Fig 6.4.3a. and 6.4.3b) are given in Table 6.4.3.

Fig 6.4.3a Double-log plot of Mn(III)-PQ-Tyr quenching effect on BSA fluorescence at 298K

Fig 6.4.3b Double-log plot of Fe(III)-PQ-Tyr quenching effect on BSA fluorescence at 298K
Table 6.4.3 Binding constant, Binding site and Binding energy values of Mn(III)/Fe(III)-PQ-Tyr 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-Tyr</td>
<td>5.18</td>
<td>1.07</td>
<td>-26.89</td>
</tr>
<tr>
<td>Fe(III)-PQ-Tyr</td>
<td>5.16</td>
<td>1.07</td>
<td>-26.88</td>
</tr>
</tbody>
</table>

The number of binding sites for both the complexes is approximated to 1, which indicates that there is one class of binding sites to metal complexes in BSA. In BSA, the tryptophan residues involved in binding could be either Trp134 or Trp212. Trp134 was embedded in the first sub-domain IB and was more exposed to a hydrophilic environment, whereas Trp212 was embedded in sub-domain IIA and deeply buried in the hydrophobic loop.\(^{17,18}\) So, from the value of n, we speculated that the metal complexes most likely binds to the hydrophobic pocket located in sub-domain IIA. The negative values of ΔG (Table 6.4.3) indicate that the binding of metal complexes to BSA is spontaneous.
6.5 Molecular docking studies of Mn(III)/Fe(III)-PQ-Tyr complexes

Molecular docking technique is an attractive scaffold to understand the Drug-BSA interactions for the rational drug design and discovery, as well as in the mechanistic study by placing a small molecule into the binding site of the BSA, which can substantiate the experimental results. The docking results revealed that the complexes Mn(III)-PQ-Tyr and Fe(III)-PQ-Tyr are located within the hydrophobic cavity of sub-domain IIA, and this is clearly illustrated in Fig 6.5.1 and 6.5.2.

Fig 6.5.1 Molecular docked model of Mn(III)-PQ-Tyr located within sub-domain IIA

Fig 6.5.2 Molecular docked model of Fe(III)-PQ-Tyr located within sub-domain IIA