Chapter 3

3.1 Introduction

The present chapter deals with the synthesis and preliminary characteristics of various ligands. For this the reaction of 5-chloromethyl-8-hydroxyquinoline (CMQ) with various bis-indoles has been adopted. The prepared bis-ligands are denoted by (3a-h).

3.2 Synthesis of bis-ligands (3a-h)

The dinegative ligand were synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline (0.1 mole) with various substituted benzaldehyde (0.1 mole), in presence of catalytic amount of sodium bicarbonate.

In a 100 mL round bottom flask was placed, a mixture of 5-chloromethyl-8-hydroxyquinoline (0.01 mole), appropriate bis-indole (0.01 mole) and aqueous sodium bicarbonate solution (5-10 ml) in 30 mL acetone. The mixture was then refluxed for 2.5 hrs with occasional stirring. The resulting mixture was then allowed to stand at room temperature. The pinkish product formed was collected by filtration, washed with water and diethyl ether and then dried in vacuum and then finally purified by recrystallization in chloroform-hexane (70:30) mixture to obtain light pink to dark red crystalline product. The preparation of bis-ligand is presented in Scheme 3.1

3.3 Experimental

As per objectives the various bis-ligands i.e. (3a-h) derivatives have been prepared. The synthesis and characterization of all the bis-ligands are summarized in this section.

3.3.1 Materials

All the chemicals used were of analytical grade which were purified by reported method. The 5-chloromethyl-8-quinolinol and various bis-indoles used were prepared by reported method which is discussed in chapter 2.
Table 3.1 The bis-indole derivatives (2a-h) used for the formation of bis-ligands

<table>
<thead>
<tr>
<th>No.</th>
<th>Bis-indole derivatives</th>
<th>General structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>3, 3’- (phenylmethylene)bis(1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>3, 3’- ((4-chlorophenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>3, 3’- ((4-nitrophenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>3, 3’- ((4-hydroxyphenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>3, 3’- ((4-methoxyphenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>3, 3’- ((4-bromophenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>3, 3’- ((4-methylphenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td>3, 3’- ((3,4-dimethylphenyl)methylene)bis (1H-indole)</td>
<td></td>
</tr>
</tbody>
</table>

Where R = C₆H₅
= 4-ClC₆H₄
= 4-NO₂C₆H₄
= 4-HOC₆H₄
= 4-CH₃OC₆H₄
= 4-BrC₆H₄
= 4-CH₃C₆H₄
= 3,4-(CH₃)₂C₆H₃
Scheme 3.1 Preparation of bis-ligands (3a-h) from bis-indole and CMQ

The structures of all the compounds (3a-h) were confirmed by analytical and spectral data.
The $^1$H NMR spectrum of compound 3a (Fig 3.1) showed twenty five aromatic protons. These twenty five aromatic protons were observed between 6.87-8.86 $\delta$ as multiplets which can be assigned to aromatic protons of quinoline, indole and phenyl moieties. The signal appeared as a singlet at 4.58 $\delta$ (4H), which is assigned to two $-\text{CH}_2-$ protons. The signal appeared as a singlet at 5.98 $\delta$ (1H) is assigned to aliphatic $-\text{CH}$ proton. A sharp signal at 11.14 $\delta$ (2H) is assigned to two aromatic hydroxyl protons, which is confirmed by D$_2$O exchange experiment.

The $^{13}$C NMR spectrum of compound 3a (Fig 3.2) showed signals at 27.10 (-$\text{CH}_2-$), 57.5 (-$\text{CH}$), 111.03, 111.89, 112.05, 117.16, 118.90, 121.58, 122.12, 123.85, 124.36, 126.86, 127.75, 128.31, 129.91, 133.31, 137.12, 139.39, 146.24, 148.20, 152.40, 153.59 $\delta$ (Ar-C). Thus total twenty two carbon signals are seen. The compound is having twenty three different types of carbon atoms and hence expected number of signals is twenty three. Experimentally the numbers of signals observed are twenty two; this may be due to overlapping of one carbon signal, which may have identical chemical shift. The DEPT-135 spectrum (Fig 3.3) showed signals at 27.10, 57.5, 111.07, 112.07, 118.89, 119.39, 121.57, 122.13, 123.90, 124.33, 128.28, 129.33, 133.28, 139.12 and 148.23 $\delta$. The spectrum showed inverted signals at 27.10 $\delta$, which are due to two symmetrical $-\text{CH}_2-$ carbons. The signals appeared at 57.5, 111.07, 112.07, 118.89, 119.39, 121.57, 122.13, 123.90, 124.33, 128.28, 129.33, 133.28, 139.12, 148.23 $\delta$ are due to fourteen tertiary carbons.

The IR spectrum of 3a (Fig 3.4) showed a broad band at 3408 cm$^{-1}$ due to $-\text{OH}$ stretching vibration. Weak band at 2930 and 2847 cm$^{-1}$ are attributed to asymmetric and symmetric stretching vibrations of methylene groups. Bands at 1580 cm$^{-1}$ are due to the C=N stretching in the ligand. The C-O stretching in the ligand may be traced to the absorptions at 1372 and 1242 cm$^{-1}$. The peak at 1230 cm$^{-1}$ in the ligand is assigned to O-H bending of the phenolic moiety. In addition to these bands, the spectrum of compound 3a has many
characteristic absorption bands which are identical to those that occur in 5,5'-methylene(8-hydroxyquinoline) (MBQ) and bis-indole\textsuperscript{5-6}.

**(3a) 5,5',-(3,3'-(phenylmethylene)bis(1H-indole-3,1-diyl) bis (methylene) diquinolin-8-ol (PBIQ)**

![Chemical structure of PBIQ]

<table>
<thead>
<tr>
<th>Molecular Formula: C\textsubscript{43}H\textsubscript{32}N\textsubscript{4}O\textsubscript{2}</th>
<th>Elemental analysis</th>
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<tr>
<td>Yield: 70%</td>
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<td>IR (KBr): $\nu_{\text{max}}$</td>
<td>$\nu$ (ppm):</td>
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<tr>
<td>1580    = C=N</td>
<td>5.98(1H, s, CH), 6.87-8.86</td>
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<tr>
<td>2930    = -CH\textsubscript{2}-</td>
<td>(25H, m, Ar-H), 11.14(2H, s, OH, D\textsubscript{2}O exchangeable).</td>
</tr>
<tr>
<td>(methylene group)</td>
<td>$\delta$ (ppm):</td>
</tr>
<tr>
<td>$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm):</td>
<td>DEPT-135:</td>
</tr>
</tbody>
</table>
(3b) 5,5,-(3,3’-(4-chlorophenylmethylene)bis(1H-indole-3,1-diyl)bis (methylene) diquinolin-8-ol (CMBQ)

Molecular Formula: C_{43}H_{31}ClN_{4}O_{2}

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<td>671.18</td>
<td>76.95</td>
<td>4.66</td>
<td>8.35</td>
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</table>

| Elemental analysis | 76.85 | 4.58 | 8.28 |

Molecular weight: 671.18
Melting Point: 232°C (Uncorrected)
Yield: 71%
IR (KBr): \( \nu_{\text{max}} \)
3401 = -OH
1593 = C=N
2938 = -CH\textsubscript{2}- (methylene group)

\textbf{1H NMR (400 MHz, DMSO-\textit{d}_6) \( \delta \) (ppm):}
4.48(4H, s, CH\textsubscript{2}), 6.08(1H, s, CH), 6.69-8.81 (24H, m, Ar-H), 10.84(2H, s, OH, D\textsubscript{2}O exchangeable).

\textbf{13C NMR (100 MHz, DMSO-\textit{d}_6) \( \delta \) (ppm):}
27.18 (-CH\textsubscript{2}-), 57.80(-CH-), 111.7, 112.06, 117.15, 118.89, 121.48, 122.08, 123.87, 124.34, 126.80, 127.72, 128.25, 129.81, 133.28, 137.10, 139.32, 146.20, 148.10, 152.34, 153.49 \( \delta \) (Ar-C).

\textbf{DEPT-135:}
27.18(-CH\textsubscript{2}-), 57.80(-CH-), 111.7, 112.04, 118.82, 119.30, 121.52, 122.54, 123.80, 124.12, 128.30, 129.15, 133.18, 139.32, 148.28.
(3c) 5,5′-(3,3′-(4-nitrophenylmethylene)bis(1H-indole-3,1-diyl)bis(methylene) diquinolin-8-ol (NIMQ)

![Chemical Structure Diagram](image)

<table>
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<tr>
<th>Molecular Formula: C_{43}H_{31}N_{5}O_{4}</th>
<th>Elemental analysis</th>
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<td>4.58</td>
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<td>10.27</td>
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<tr>
<td>3400 = -OH</td>
<td>%H</td>
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<tr>
<td>1586 = C=N</td>
<td>4.45</td>
</tr>
<tr>
<td>2932 = -CH_{2}- (methylene group)</td>
<td>10.25</td>
</tr>
</tbody>
</table>

1H NMR (400 MHz, DMSO-d_{6}) δ_{H} (ppm):
- 4.36 (4H, s, CH_{2})
- 6.03 (1H, s, CH)
- 6.64–8.84 (24H, m, Ar-H)
- 10.94 (2H, s, OH, D_{2}O exchangeable)

13C NMR (100 MHz, DMSO-d_{6}) δ_{c} (ppm):
- 27.12 (-CH_{2}-)
- 57.49 (-CH-)
- 111.07, 112.06, 117.15, 118.89, 121.48, 122.08, 123.87, 124.34, 126.80, 127.72, 128.25, 129.81, 133.28, 137.10, 139.32, 146.20, 148.10, 152.34, 153.49 δ (Ar-C).

DEPT-135: 27.10 (-CH_{2}-), 57.48 (-CH-), 111.07, 112.04, 117.14, 118.88, 121.55, 122.10, 123.87, 124.30, 128.24, 129.30, 133.24, 139.34, 148.12.
(3d) \(5,5',-(3,3'-(4\text{-Hydroxyphenylmethylene})\text{bis}(1H\text{-indole-3,1-diyl})\text{bis (methylene)}\text{ diquinolin-8-ol (HMBIQ)}\)

\[
\text{Molecular Formula: } C_{43}H_{32}N_4O_3
\]

\[
\begin{array}{|c|c|c|}
\hline
\text{Elemental analysis} & \text{Calculated} & \text{Found} \\
\%\text{H} & 4.94 & 4.86 \\
\%\text{N} & 8.58 & 8.49 \\
\%\text{O} & 79.12 & 79.02 \\
\hline
\end{array}
\]

\[
\text{Molecular weight: } 652.74
\]

\[
\text{Melting Point: } 238^\circ C \text{ (Uncorrected)}
\]

\[
\text{Yield: } 72\%
\]

\[
\text{IR (KBr): } \nu_{\text{max}}
\]

\[
\begin{align*}
3404 & = -\text{OH} \\
1566 & = -\text{C=N} \\
2954 & = -\text{CH}_2-
\end{align*}
\]

\[
\text{Methylene group)
}\]

\[
\begin{array}{|c|}
\hline
\text{NMR (400 MHz, DMSO-\text{d}_6) } \delta_{\text{H}} \text{ (ppm)}: \\
4.69(4\text{H, s, CH}_2), 6.13(1\text{H, s, CH}), 6.67-9.27 \\
(24\text{H, m, Ar-H}), 10.3(3\text{H, s, OH, D}_2\text{O exchangeable}).
\hline
\end{array}
\]

\[
\begin{array}{|c|}
\hline
\text{NMR (100 MHz, DMSO-\text{d}_6) } \delta_{\text{C}} \text{ (ppm)}: \\
27.92(-\text{CH}_2-), 57.59(-\text{CH}-), 111.08, 111.90, \\
115.77, 118.77, 119.63, 121.60, 122.13, \\
123.80, 123.99, 124.56, 126.91, 127.78, \\
128.29, 129.32, 133.35, 137.07, 139.35, \\
146.95, 148.23, 152.40, 153.98(\text{Ar-C}).
\hline
\end{array}
\]

\[
\text{DEPT-135: } 27.92(-\text{CH}_2-), 57.59(-\text{CH}-), \\
111.09, 111.90, 118.77, 119.63, 121.43, \\
122.13, 123.80, 123.99, 128.29, 129.33, \\
133.35, 148.23
\]
(3e) 5,5,-(3,3’-(4-Methoxyphenylmethylene)bis(1H-indole-3,1-diyldiyl)bis (methylene) diquinolin-8-ol (MBIMQ)

Molecular Formula: C_{44}H_{34}N_{4}O_{3}  
Elemental analysis

<table>
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<th>%H</th>
<th>%N</th>
</tr>
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<tr>
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<td>Calculated 76.26</td>
<td>5.14</td>
<td>8.40</td>
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<td>Melting Point: 235°C (Uncorrected)</td>
<td>Found 76.20</td>
<td>5.08</td>
<td>8.36</td>
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<tr>
<td>Yield: 75%</td>
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<tr>
<td>IR (KBr): υ_{max}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3410 = -OH</td>
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</tr>
<tr>
<td>1583 = C=N</td>
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<td></td>
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</tr>
<tr>
<td>2934 = -CH_{2-}</td>
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<tr>
<td>(methylene group)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

{\textbf{1H NMR (400 MHz, DMSO-\textit{d}6) \ δ_\text{H} (ppm):}}
3.86 (3H,s,CH₃), 4.68(4H, s, CH₂), 5.77(1H, s, CH), 6.68- 8.85(24H, m, Ar-H), 10.83(2H, s, OH, D₂O exchangeable).

{\textbf{13C NMR (100 MHz, DMSO-\textit{d}6) \ δ_\text{c} (ppm):}}
27.89(-CH₂-), 56.13(-CH₃), 55.38(-CH-), 111.07, 111.89, 114.98, 118.90, 119.62, 121.40, 121.83, 122.12, 123.79, 123.91, 126.90, 133.35, 137.09, 139.34, 146.25, 148.23, 152.39, 153.61(Ar-C).

{\textbf{DEPT-135:}}
27.90(-CH₂-), 56.16(-CH₃), 55.38(-CH-), 111.08, 111.89, 118.75, 119.62, 121.83, 122.13, 123.79, 123.91, 128.27, 129.66, 133.35, 148.23
(3f) 5,5-\(\text{-}(3,3'-(4\text{-bromophenyl})\text{methylene})\text{bis}(1H\text{-indole-3,1-diyl})\text{bis (methylene)}\text{ diquinolin-8-ol (BMBIQ)}

\[
\begin{array}{c}
\text{Molecular Formula: } \text{C}_{43}\text{H}_{31}\text{BrN}_{4}\text{O}_{2} \\
\text{Elemental analysis} \\
\text{Molecular weight: } 714.64 \\
\text{Melting Point: } 236-238^\circ \text{C (Uncorrected)} \\
\text{Yield: 74\%} \\
\text{IR (KBr): } \nu_{\text{max}} \\
3405 = -\text{OH} \\
1577 = \text{C=N} \\
2945 = -\text{CH}_2\text{-} \\
\text{(methylene group)}
\end{array}
\]

\[
\begin{array}{c|c|c|c}
\text{Calculated} & \% \text{C} & \% \text{H} & \% \text{N} \\
\text{Found} & 72.1\% & 4.37 & 7.83 \\
& 72.08 & 4.30 & 7.74 \\
\end{array}
\]

\[\delta_{\text{H}} \text{ (ppm):} \\
4.54(4\text{H, s, } \text{CH}_2), 6.06(1\text{H, s, } \text{CH}), 6.88-8.85(24\text{H, m, Ar-H}), 11.12(2\text{H, s, } \text{OH, D}_2\text{O exchangeable})
\]

\[\delta_{\text{C}} \text{ (ppm):} \\
27.8(-\text{CH}_2\text{-}), 57.12(-\text{CH}_-, ) 111.12, 111.92, 115.79, 118.77, 119.63, 121.60, 122.13, 123.80, 123.99, 124.56, 126.99, 127.88, 128.35, 129.42, 133.35, 137.27, 140.15, 146.90, 148.28, 152.55, 153.58(\text{Ar-C}).
\]

\text{DEPT-135:} 27.80(-\text{CH}_2\text{-}), 57.10(-\text{CH}_-, ) 111.11, 111.90, 118.77, 119.60, 121.43, 122.10, 123.80, 123.96, 128.29, 129.30, 133.32, 148.23.
(3g) \(5,5'-(3,3'-(p\text{-}tolylmethylene)\text{bis}(1\text{-}H\text{-}indole-3,1-diyl)\text{bis}(methylen)e\text{ diquinolin-8-ol\ (TBIMQ)}}\)

Molecular Formula: \(C_{44}H_{34}N_{4}O_{2}\)  

<table>
<thead>
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<tr>
<td>Found</td>
<td>81.18</td>
<td>5.15</td>
<td>8.54</td>
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</table>

\(^1\text{H NMR\ (400 MHz, DMSO-\text{d}_6\)  }\delta_{H\ (ppm)}:\)

- 2.35(3H, s, CH3), 4.81(4H, s, CH2), 6.09(1H, s, CH), 6.87-8.84(24H, m, Ar-H), 10.74(2H, s, OH, D\text{2O exchangeable}).

\(^{13}\text{C NMR\ (100 MHz, DMSO-\text{d}_6\)  }\delta_{c\ (ppm)}:\)

- 22.6 (-CH3), 27.90(-CH2-), 55.45(-CH-), 111.17, 111.88, 114.96, 118.92, 119.64, 121.42, 121.90, 122.32, 123.89, 124.01, 127.40, 133.45, 137.19, 139.44, 145.25, 149.13, 152.89, 153.21(Ar-C).

\textbf{DEPT-135:} 27.90(-CH2-), 56.16(-CH3), 55.38(-CH-), 111.16, 111.89, 118.90, 119.62, 121.43, 122.30, 123.85, 124.01, 127.27, 133.35, 145.25, 148.23.
(3h) 5,5,-(3,3’-(3,4-diphenyl)methylene) bis(1H-indole-3,1-diyl)bis (methylene) diquinolin-8-ol (DBIMQ)

![Chemical Structure]

**Molecular Formula:** C_{45}H_{36}N_{4}O_{2}

**Elemental analysis**

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**Molecular weight:** 664.79

**Melting Point:** 228°C (Uncorrected)

**Yield:** 70%

**IR (KBr):**
- ν_{max} 3401 = -OH
- 1512 = C=N
- 2944 = -CH_{2}- (methylene group)

**¹H NMR (400 MHz, DMSO-d_{6}) δ H (ppm):**
- 2.15(6H, s, CH_{3}), 4.68(4H, s, CH_{2}), 6.02(1H, s, CH), 6.89-8.82 (23H, m, Ar-H), 10.64(2H, s, OH, D_{2}O exchangeable).

**¹³C NMR (100 MHz, DMSO-d_{6}) δ c (ppm):**
- 21.4 (m-CH_{3}), 22.5 (p-CH_{3}), 27.92(-CH_{2}-), 55.51(-CH-), 111.14, 111.80, 115.06, 118.82, 119.84, 121.32, 121.90, 122.30, 123.92, 124.21, 128.40, 133.40, 137.29, 138.44, 146.25, 148.13, 152.86, 153.42(Ar-C).

**DEPT-135:**
- 27.90(-CH_{2}-), 56.16(-CH_{3}), 55.38(-CH-), 111.16, 111.89, 118.82, 119.86, 121.43, 122.30, 123.85, 124.20, 128.27, 133.35, 146.24, 148.16.
**Fig. 3.1** The $^1$H NMR spectrum of Compound 3a

**Fig. 3.2** The $^{13}$C NMR spectrum of Compound 3a
**Fig. 3.3** DEPT-135 of compound 3a

**Fig. 3.4** FT-IR of compound 3a
**Fig. 3.5** The $^1$H NMR spectrum of Compound 3b

**Fig. 3.6** The $^{13}$C NMR spectrum of Compound 3b
Fig. 3.7 FT-IR of compound 3b

Fig. 3.8 The $^1$H NMR spectrum of Compound 3c
Fig. 3.9 The $^{13}$C NMR spectrum of Compound 3c

Fig. 3.10 FT-IR of compound 3c
**Fig. 3.11** The $^1$H NMR spectrum of Compound 3d

**Fig. 3.12** The $^{13}$C NMR spectrum of Compound 3d
**Fig 3.13** DEPT-135 of comp 3d

**Fig. 3.14** The $^1$H NMR spectrum of Compound 3e
Fig. 3.15 The $^{13}$C NMR spectrum of Compound 3e

Fig 3.16 DEPT-135 of comp 3e
**Fig. 3.17** The $^1$H NMR spectrum of Compound 3f

**Fig. 3.18** The $^{13}$C NMR spectrum of Compound 3f
Fig. 3.19 FT-IR of compound 3f

Fig. 3.20 The $^1$H NMR spectrum of Compound 3g
Fig. 3.21 The $^{13}$C NMR spectrum of Compound 3g

Fig.3.22 $^1$HNMR spectrum of compound 3h
Fig. 3.23 $^{13}$C NMR spectrum of compound 3h

Fig. 3.24 FT-IR of compound 3h

References
[1] A. I. Vogel


