Experimental METHODS

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3.1 Introduction

This chapter deals with the experimental procedures adopted for the synthesis of the intermediates and target compounds. The types of material used, their purification steps, methods of preparation of intermediates, different steps involved in the synthesis of hole and electron transporting materials and brief description of various analytical instrumental techniques used for characterization are discussed in detail.

3.2 Materials

Annular (AR) and laboratory grade (LR) reagents were purchased and used accordingly for synthetic work. Common solvents used for working up of the reactions were of commercial grade and were used after purification according to the procedure in literature.

3.2.1 Solvents

Solvents used for synthetic works such as acetone, benzene, cyclohexane, 1,2–dichlorobenzene and terahydrofuran (E. Merck, India) were purified according to the standard procedure given by Vogel and Armaarego [282, 283]. Solvents such as diethyl ether, ethyl alcohol, ethyl acetate, hexane, methyl alcohol, etc were used for chromatography and for the working of the reactions were of commercial grade and distilled twice, before use.

Spectroscopic grade chloroform, carbon tetra chloride, dimethylformamide, ethyl alcohol, methyl alcohol (E. Merck, India) was used for UV-Visible and Fluorescence spectrometric analysis. These solvents were used without further purification. Deuterated chloroform (CDCl$_3$. 99.8% containing 0.03 v/v of tetramethyl silane (TMS), Deuterated dimethyl sulphoxide (DMSO-d6, containing 0.03 v/v of TMS) trifluoro acetic acid (TFA) (Aldrich) were used as solvents for recording
nuclear magnetic resonance (NMR) spectra of the samples. Potassium bromide (KBr) (E. Merck, India) was used for fourier transfer infra red (FT-IR) spectroscopy measurements. In cyclic voltametry (CV) glassy carbon was used as electrode and acetonitrile (ACN) containing 0.1M of supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF₆) were used as solvents.

3.2.2 Reagents

3.2.2.1. Common reagents

1. p-Phenylenediamine: (E. Merck, India), white (tan when impure) solid, recrystallized with ethyl alcohol and used, Melting point (Mp): 143°C.
2. Resorcinol (AR) (Benzene-1,3-diol): (E. Merck, India), white solid used as received. Mp: 110°C.
3. Ethyl acetoacetate (AR): (E. Merck, India), colourless liquid. Boiling point (Bp): 180.8°C.
4. N-bromosuccinimide (C₄H₄BrNO₂): (Loba Chemie), Mp: 183°C, light yellow solid, recrystallized from boiling water, dried with CaCl₂ and used.
5. Tetrabutylammoniumbromide (TBAB, C₁₆H₃₆BrN): (Loba Chemie), Mp: 119°C, Dried over P₂O₅ under vacuum and used.
6. β-Naphthol (C₁₀H₈-OH): (E. Merck, India), Mp: 144°C, pink flake solid, recrystallized from boiling ethanol and used.
7. p Bromoanisole (AR): (E. Merck, India), Bp: 223°C, clear to slightly yellow liquid used as such.

3.2.2.2. Specific reagents

1. 1-bromoethane (C₂H₅-Br): (Loba Chemie), Bp: 65°C, d: 1.460, colourless liquid
2. n- Amyl bromide (n -Pentyl bromide, C₅H₁₁-Br): (Loba Chemie), colorless liquid, Bp 129°C, d: 1.218
3. Bromobenzene (C₆H₅Br): (Loba Chemie), Bp: 155.9°C, d: 1.495
4. 1-Bromopropane (C\textsubscript{3}H\textsubscript{7}-Br): (Loba Chemie), Bp: 71°C, d: 1.354, colorless liquid
5. n-Butyl bromide (C\textsubscript{4}H\textsubscript{9}-Br): (Loba Chemie), Bp: 101°C d: 1.267, colorless liquid

All the above specific reagents were purified as follows. Washed vigorously with conc. sulphuric acid, and then with 10% sodium carbonate and water, dried with calcium chloride, distilled and used.

3.3. Preparation of intermediate compounds

3.3.1. 1- Bromo-2-naphthol (A)

1-Bromo-2-naphthol was prepared by stirring 2-naphthol (0.01 mol, 1.442 g) with N-bromosuccinimide (NBS) (0.0105 mol, 1.869 g) and 10 mol % ammonium acetate (0.7734 g) in 10 ml methyl cyanide at room temperature for 1.0 minute. Product was extracted using ethyl acetate and recrystallized from toluene [284]. Scheme 3.1 represents route and structure for the synthesis of 1-bromo-2 naphthol. The structure of the compound was characterized by FT-IR and NMR spectroscopic methods. Appearance: Brown Solid, Yield: 95.55%, Mp: 78°C.

In FT-IR spectrum the main characteristic peaks are at 3269 cm\textsuperscript{-1} (OH stretching), 3071 cm\textsuperscript{-1} (aromatic -CH stretching), 858 cm\textsuperscript{-1} (-CH deformation for 1,2-disubstituted benzene ring), 557 cm\textsuperscript{-1} (C-Br stretching). In proton NMR spectrum peaks are observed at 6.79-7.98 ppm (six aromatic protons) and 4.35 ppm (hydrogen of-OH).

\[
\begin{align*}
\text{NBS / MeCN} & \quad \text{Ammonium acetate} \\
\text{OH} & \quad \text{Br} \\
\text{A} & \quad \text{OH}
\end{align*}
\]

*Scheme 3.1: Synthetic scheme for 1-Bromo-2 Naphthol (A)*
3.3.2. **Bromo alkoxy naphthalene (B-E)**

Substitution reaction was carried out by refluxing 1-bromo-2-sodium naphthoate (0.01 mol, 2.450 g), n-alkyl bromide (0.01 mol) and 25 ml toluene in presence of 0.967 g (0.003 mol) tetrabutyl ammonium bromide (TBAB) for 4.0 hours at 70°C to get 1-bromo-2-alkoxy naphthalene. The product was extracted using 3:1 toluene – water system and distilled under reduced pressure. Product obtained was recrystallized from toluene [285]. Ethyl bromide, n-propyl bromide, n-butyl bromide and n-pentyl bromide were used as alkyl bromide to get corresponding alkoxy naphthalenes. Scheme 3.2 represents route and structures for the synthesis of 1-bromo-2-alkoxy naphthalenes. The structures of prepared compounds were characterized by FT-IR and NMR spectroscopic methods.

![Scheme 3.2: Synthetic scheme for Bromo alkoxy naphthalene (B-E)](image)

### 3.3.2.1. **1-Bromo-2-ethoxy naphthalene (B):**

Appearance: brown solid. Yield: 75.70%, Mp: 65°C.

FT-IR (KBr, υ cm⁻¹): 3058, 2879, 1379, 1217, 574.

In FT-IR spectrum, the main characteristic peak at 3269 cm⁻¹ (-OH stretching) of the reactant 1-bromo-2-naphthol disappears which confirms the formation of –OC₂H₅. Appearance of peaks at 2879 cm⁻¹ (-CH stretching of -C₂H₅), 1379 cm⁻¹ (-CH deformation of -C₂H₅), 1217 cm⁻¹ (C-O-C stretching) also confirms the formation of ethoxy group and peaks
also appear at 3058 cm\(^{-1}\) (aromatic -CH stretching), 574 cm\(^{-1}\) (C-Br stretching).

In proton NMR spectrum, peaks are observed at 6.97-8.10 ppm (six aromatic hydrogen) and 1.33-4.08 ppm (five hydrogen of -OC\(_2\)H\(_5\)).

3.3.2.2. 1-Bromo-2-propoxy naphthalene (C):

Appearance: light brown liquid, Yield: 65.25\%, Bp: 205\(^\circ\)C.

FT-IR (KBr, \(\nu\) cm\(^{-1}\)): 3055, 2871, 1456, 1215, 575.

In FT-IR spectrum, the main characteristic peak at 3269 cm\(^{-1}\) (-OH stretching) of the reactant 1-bromo-2-naphthol disappears which confirms the formation of –OC\(_3\)H\(_7\). Appearance of peaks at 2871 cm\(^{-1}\) (-CH stretching of –C\(_3\)H\(_7\)), 1456 cm\(^{-1}\) (-CH deformation of –C\(_3\)H\(_7\)), 1215 cm\(^{-1}\) (C-O-C stretching) also confirms the formation of propoxy group and peaks also appear at 3055 cm\(^{-1}\) (aromatic -CH stretching), 575 cm\(^{-1}\) (C-Br stretching).

In proton NMR spectrum, peaks are observed at 6.97-8.11 ppm (six aromatic hydrogen) and 0.92-4.08 ppm (seven hydrogen of-OC\(_3\)H\(_7\)).

3.3.2.3. 1-Bromo-2-butoxy naphthalene (D):

Appearance: brown liquid, Yield: 63.52\%, Bp: 220\(^\circ\)C.

FT-IR (KBr, \(\nu\) cm\(^{-1}\)): 3056, 2871, 1387, 1217, 573. In FT-IR spectrum, the main characteristic peak at 3269 cm\(^{-1}\) (-OH stretching) of the reactant 1-bromo-2-naphthol disappears which confirms the formation of –OC\(_4\)H\(_9\). Appearance of peaks at 2871 cm\(^{-1}\) (CH stretching of –C\(_4\)H\(_9\)), 1456 cm\(^{-1}\) (-CH deformation of –C\(_4\)H\(_9\)), 1217 cm\(^{-1}\) (C-O-C stretching) also confirms the formation of butoxy group and peaks also appear at 3055 cm\(^{-1}\) (aromatic -CH stretching), 575 cm\(^{-1}\) (C-Br stretching).

In proton NMR spectrum, peaks are observed at 6.79-8.5 ppm (six aromatic hydrogen) and 0.89-4.09 ppm (eleven hydrogen of-OC\(_5\)H\(_{11}\)).
3.3.2.4. **1-Bromo-2-pentoxy naphthalene (E):**

Appearance: brown liquid, Yield: 67.80%, Bp: 234°C.

FT-IR (KBr, $\nu$ cm$^{-1}$): 3057, 2859, 1478, 1217, 578. In FT-IR spectrum, the main characteristic peak at 3269 cm$^{-1}$ (-OH stretching) of the reactant 1-bromo-2-naphthol disappears which confirms the formation of $\text{-OC}_5\text{H}_{11}$. Appearance of peaks at 2859 cm$^{-1}$ (CH stretching of $\text{-C}_5\text{H}_{11}$), 1478 cm$^{-1}$ (-CH deformation of $\text{-C}_5\text{H}_{11}$), 1217 cm$^{-1}$ (C-O-C stretching) also confirms the formation of pentoxy group and peaks also appear at 3057 cm$^{-1}$ (aromatic -CH stretching), 578 cm$^{-1}$ (C-Br stretching).

In proton NMR spectrum, peaks are observed at 6.79-8.5 ppm (six aromatic hydrogen) and 0.89-4.09 ppm (eleven hydrogen of $\text{-OC}_5\text{H}_{11}$).

3.3.3. **7-Hydroxy-4-methylcoumarin (F)**

A mixture of Resorcinol (10.03 g, 0.091 mol) and ethylacetoacetate (13.05 mL, 0.103 mol) was added drop-wise to 50 ml of concentrated sulphuric acid maintaining at a temperature below 5°C. The mixture was stirred for two hours for the same temperature and kept at room temperature for 24 hours. It was then poured into ice (300 g), filtered and the precipitate obtained was washed with cold water. The precipitate was dissolved in 15 ml of 5% sodium hydroxide. The yellow solution thus obtained was neutralized with dilute sulphuric acid. The Crude product was recrystallized from 95% ethanol [286].

Scheme 3.3 represents route for the synthesis of 7-hydroxy-4-methyl coumarin.
Experimental

Scheme 3.3: Synthetic scheme for 7-hydroxy 4-methyl coumarin (F)

Appearance: Colourless crystals; yield: 88.25%; Mp: 183°C;
UV-Vis. (Ethanol, nm): 358, 302, 255;
FT-IR (KBr, \( \nu \) cm\(^{-1} \)): 3513, 2424, 1742, 1622, 1608, 1463, 1250;
\(^1\)H-NMR (CDCl\(_3\), \( \delta \)): 2.417 (methyl, 3H, s), 6.648 (Ar, 1H, d), 8.101 (Ar, 1H, d), 5.855 (Ar, 1H, s), 6.67 (Ar, 1H, s), 4.83 (hydroxyl, 1H, s);
\(^13\)C-NMR (CDCl\(_3\), ppm): 56, 119.8, 119.1, 119.5, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2.

3.3.4. Bromo-7-hydroxy-4-methylcoumarin (G)

7-Hydroxy-4-methylcoumarin (F) (5.705 g, 0.0324 mol), 30 mL acetonitrile and 10 mol% Ammonium acetate (0.7734 g) were taken in a round bottomed flask. N-bromosuccinimide (8.65 g, 0.0486 mol) was added slowly with constant stirring at room temperature for 45 minutes. Completion of reaction was checked by thin layer chromatography (TLC). Product formed was extracted using ethyl acetate-water mixture. Purification was done by means of column chromatography using ethyl acetate: hexane (1:4) mixture as eluent and it was recrystallized from ethanol [284]. Scheme 3.4 represents route and structures for the synthesis of bromo-7-hydroxy-4-methyl coumarin.
Experimental

Scheme 3.4: Synthetic scheme for bromo-7-hydroxy 4-methyl coumarin (G)

Appearance: brown solid; Yield: 75.75%; Mp: 158°C;
UV-Vis. (Ethanol, nm): 458, 323, 220
FT-IR (KBr, υ cm⁻¹): 3431, 2989, 2425, 1775, 1617, 1250, 640
¹H-NMR (CDCl₃, δ): 2.417 (methyl, 3H, s), 6.648 (ArH, 1H, d), 8.101 (ArH, 1H, d), 6.67 (ArH, 1H, s), 5.05 (hydroxyl, 1H, s);
¹³C-NMR (CDCl₃, ppm): 161.8, 156.7, 153.2, 150.8, 125.6, 114.2, 112.3, 107.5, 102.2, 19.4.

3.3.5. N, N’-Diphenylbenzene-1,4-diamine (H)

1,4-Phenylene diamine (5.407 g, 0.05 mol), bromobenzene (10.54 mL, 0.1 mol), CuCl (0.022 g, 0.0002 mol) and 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25 ml of acetone for 14 hours at 60°C. Completion of the reaction was checked by TLC. The solvent was evaporated in vacuum and extracted using ether. It was washed with 10% brine solution, dried over sodium bisulphite and concentrated to give a yellow residue which was purified by column chromatography. It was recrystallized from ethanol [287]. Scheme 3.5 represents route and structures for the synthesis of N,N’-Diphenylbenzene-1,4-diamine.
Scheme 3.5: Synthetic scheme for N, N'-Diphenyl-Benzene-1, 4-Diamine (H)

Appearance: Yellow solid; Mp: 135°C, Yield: 64.40%.
UV-Vis. (Ethanol, nm): 365, 321, 298
FT-IR (KBr, υ cm⁻¹): 3465, 3337, 3207, 1625, 1517, 1305, 837, 514
¹H-NMR (CDCl₃, δ): 6.21-7.01(14H, ArH), 4.56(2H, NH)
¹³C-NMR (CDCl₃, ppm): 143.2 (2C,-C-NH), 132.7 (2C, -C-NH), 117.9-129.4 (14C, Ar)

3.4. Synthesis of Hole and Electron transporting material

Phenylene diamine based spiro shaped compounds fulfill all required properties that is needed for the fabrication of optoelectronic devices. Synthesis of such compounds includes the coupling reaction between halo and amino compounds. Here we used simple Ullmann coupling using CuCl as catalyst [288, 289]. CuCl is used because of low cost and easy availability. Four series of compounds are synthesized. Each series contains derivatives of ethyl, propyl, butyl and penty groups. Among the compounds, three series of compounds are hole transporting and one series of compound act both as hole and electron transporting. So these compounds have been used to fabricate both solid state DSSC and Hybrid OLED.

3.4.1. Synthesis of Series I Compounds

3.4.1.1. Synthesis of 7-alkoxy 3-bromo 4-methylcoumarin (I-L)
3-Bromo-7-hydroxy-4-methylcoumarin (3.048 g, 0.012 mol), alkyl bromide (0.12 mol), 7.0 g of potassium carbonate (dried at 110°C) and 25 ml of acetone were refluxed at 70°C for 48 hours. Completion of the reaction was checked by TLC. The solvent was evaporated in vacuum and extracted using dichloromethane. It was washed with 10% brine solution, dried over sodium bisulphite and concentrated to give a brown residue which was purified by column chromatography. It was recrystallized from methanol [290]. Ethyl bromide n-propyl bromide, n-butyl bromide and n-pentyl bromide were used as alkyl bromide to get corresponding alkoxy naphthalene. Scheme 3.6 represents route and structures for the synthesis of 7-alkoxy 3-bromo 4-methyl coumarin.

\[
\text{Scheme 3.6: Synthetic scheme for 7-alkoxy 3-bromo 4-methyl coumarin (I-L)}
\]

Table 3.1 gives the yield and physical data of 7-alkoxy 3-bromo 4-methyl coumarin (I-L)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>72</td>
<td>60.04</td>
<td>48</td>
<td>Brown solid</td>
</tr>
<tr>
<td>J</td>
<td>78</td>
<td>64.57</td>
<td>48</td>
<td>Dark brown solid</td>
</tr>
<tr>
<td>K</td>
<td>80</td>
<td>62.13</td>
<td>48</td>
<td>Brown Solid</td>
</tr>
<tr>
<td>L</td>
<td>75</td>
<td>58.90</td>
<td>48</td>
<td>Light brown Solid</td>
</tr>
</tbody>
</table>

I: 3-bromo-7-ethoxy-4-methyl coumarin, J: 3-bromo-7-propoxy-4-methyl coumarin, K: 3-bromo-7-butoxy-4-methyl coumarin, L: 3-bromo-7-pentoxy-4-methyl coumarin
3.4.1.2 Synthesis of 3,3’-(1,4-phenylene bis (phenylazanediyl)) bis-(7-alkoxy-4-methyl-2H-chromen-2-one) (Series I)

N,N’-Diphenyl-benzene-1,4-diamine (H) (13.0 g, 0.05 mol), 7-alkoxy-3-bromo-4-methyl coumarin (I-L) (0.1 mol), CuCl (0.022 g, 0.0002 mol), 1.0g ( 0.005 mol) of 1,10 phenanthroline, 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25ml dichlorobenzene for 18 hours at 170°C in oil bath under nitrogen atmosphere. Completion of the reaction was checked by TLC [291]. Scheme 3.7 represents route and structures for the synthesis of 3,3’-(1,4-phenylene bis (phenylazanediyl)) bis (7-ethoxy-4-methyl-2H-chromen-2-one) (Series I).

Scheme 3.7: 3,3’-(1,4-phenylenebis(phenylazanediyl))bis(7-alkoxy-4 methyl-2H-chromen-2-one) (Series I)
After removal of the solvent under vacuum, ammonia solution (50 ml) was added and the mixture was left to stand for 2.0 hours. Ethyl acetate (150 ml) and water (100 ml) were added to the mixture. The organic phase was separated, washed with water (100 ml×2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, filtered and the solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate: hexane (1:4) as eluent to obtain brown solid which was recrystallized from hexane.

Table 3.2 gives the physical data of 3,3’-(1,4-phenylene bis (phenylazanediyl)) bis (7-alkoxy-4-methyl-2H-chromen-2-one) (Series I).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactant</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEC</td>
<td>I</td>
<td>109</td>
<td>40.15</td>
<td>18</td>
<td>Brown needles</td>
</tr>
<tr>
<td>PPPC</td>
<td>J</td>
<td>115</td>
<td>40.11</td>
<td>18</td>
<td>Dark Yellow needles</td>
</tr>
<tr>
<td>PPBC</td>
<td>K</td>
<td>112</td>
<td>39.90</td>
<td>17</td>
<td>Brown needles</td>
</tr>
<tr>
<td>PPPEC</td>
<td>L</td>
<td>102</td>
<td>38.95</td>
<td>19</td>
<td>Light brown needles</td>
</tr>
</tbody>
</table>

**PPEC**: 3,3’-(1,4-phenylenebis(phenylazanediyl))bis(7-ethoxy-4-methyl-2H-chromen-2-one); **PPPC**: 3,3’-(1,4-phenylenebis(phenylazanediyl))bis(7-propoxy-4-methyl-2H-chromen-2-one); **PPBC**: 3,3’-(1,4-phenylenebis(phenylazanediyl))bis(7-butoxy-4-methyl-2H-chromen-2-one); **PPPEC**: 3,3’-(1,4-phenylenebis(phenylazanediyl))bis(7-pentoxy-4-methyl-2H-chromen-2-one)

### 3.4.2. Synthesis of Series II Compounds

#### 3.4.2.1. Synthesis of N,N’-bis-(2-alkoxy-naphthalen-1-yl)-N,N’-diphenyl benzene-1,4-diamine (Series II)

N,N’-Diphenyl benzene-1,4-diamine (H) (13.01g, 0.05mol), bromo alkoxy naphthalene (B-E) (0.1mol), CuCl (0.022g, 0.0002mol), 1g of 1,10
phenanthroline (0.005 mol), 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25 ml dichlorobenzene for 20 hours at 170°C in oil bath under nitrogen atmosphere. Completion of the reaction was checked by TLC.

Scheme 3.8 represents route and structures for the synthesis of N,N’-Bis-(2-alkoxy-naphthalen-1-yl)-N,N'-diphenyl benzene-1,4-diamine (Series II). After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2.0 hours. Ethyl acetate (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water (100 mL×2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and the solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate : hexane (1:4) as eluent to obtain dark yellow solid which was recrystallized from ethanol-hexane mixture.
Table 3.3: Physical data of N,N’-Bis-(2-alkoxy naphthalen-1-yl)-N,N’-diphenyl benzene-1,4-diamine (Series II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactant</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENDB</td>
<td>B</td>
<td>93</td>
<td>56.59</td>
<td>18</td>
<td>Dark yellow crystals</td>
</tr>
<tr>
<td>PNDB</td>
<td>C</td>
<td>89</td>
<td>54.60</td>
<td>20</td>
<td>Light yellow needles</td>
</tr>
<tr>
<td>BNDB</td>
<td>D</td>
<td>85</td>
<td>49.55</td>
<td>22</td>
<td>Yellow needles</td>
</tr>
<tr>
<td>PENDB</td>
<td>E</td>
<td>76</td>
<td>47.40</td>
<td>20</td>
<td>Yellow crystals</td>
</tr>
</tbody>
</table>

**ENDB:** N,N’-Bis-(2-ethoxy-naphthalen-1-yl)-N,N’-diphenyl-benzene-1,4-diamine, **PNDB:** N,N’-Bis-(2-propoxy-naphthalen-1-yl)-N,N’-diphenyl-benzene-1,4-diamine, **BNDB:** N,N’-Bis-(2-butoxy-naphthalen-1-yl)-N,N’-diphenyl-benzene-1,4-diamine, **PENDB:** N,N’-Bis-(2-pentoxy-naphthalen-1-yl)-N,N’-diphenyl benzene-1,4-diamine

Table 3.3 gives the physical data of N,N’-bis-(2-alkoxy-naphthalen-1-yl)-N,N’-diphenyl benzene-1,4-diamine (Series II).

### 3.4.3. Synthesis of Series III Compounds

#### 3.4.3.1. Synthesis of N,N’-Bis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (M-P)

1,4-Phenylene diamine (5.407 g, 0.05 mol), Bromo alkoxy naphthalene (B-E) (0.1 mol), CuCl (0.022 g, 0.0002 mol), 1.0 g of 1,10-phenanthroline (0.005 mol), 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25 ml dichlorobenzene for 22 hours at 170°C in oil bath under nitrogen atmosphere. Completion of the reaction was checked by TLC. After removal of the solvent in vacuo, ammonia solution (50 ml) was added and the mixture was left to stand for 2.0 hours. Ethyl acetate (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml×2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, filtered and
Experimental

The solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate: hexane (1:4) as eluent to obtain dark yellow solid which was recrystallized from hexane.

Table 3.4: Physical data of N,N'-bis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (M-P)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>69</td>
<td>60.75</td>
<td>22</td>
<td>Brown crystals</td>
</tr>
<tr>
<td>N</td>
<td>72</td>
<td>64.58</td>
<td>20</td>
<td>Dark brown solid</td>
</tr>
<tr>
<td>O</td>
<td>68</td>
<td>62.19</td>
<td>21</td>
<td>Brown Solid</td>
</tr>
<tr>
<td>P</td>
<td>75</td>
<td>58.95</td>
<td>22</td>
<td>Light brown crystals</td>
</tr>
</tbody>
</table>

M: N,N'-Bis-(2-ethoxy-naphthalen-1-yl)-benzene-1,4-diamine, N: N,N'-Bis-(2-propoxy-naphthalen-1-yl)-benzene-1,4-diamine, O: N,N'-Bis-(2-butoxy-naphthalen-1-yl)-benzene-1,4-diamine, P: N,N'-Bis-(2-pentoxy-naphthalen-1-yl)-benzene-1,4-diamine

Table 3.4 gives the physical data of N,N'-Bis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (M-P).

Figure 3.9 represents route and structures for the synthesis of N,N'-bis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (M-P).
3.4.3.2. Synthesis of $N,N,N',N'$-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (Series III)

Bromo alkoxy naphthalene (B-E) (0.1 mol), $N,N',N'$-bis-(2-alkoxy naphthalen-1-yl) benzene-1,4-diamine (M-P) (0.05 mol), CuCl (0.0220 g, 0.0002 mol), 1.0 g of 1,10-phenanthroline, 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25 ml dichlorobenzene for 22 hours at 170°C under nitrogen atmosphere. Completion of the reaction was checked by TLC. After removal of the solvent in vacuo, ammonia solution (50 ml) was added and the mixture was left to stand for 2.0 hours. Ethyl acetate (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml×2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, filtered and the solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate – hexane as eluent to obtain dark brown solid which was recrystallized from hexane.
Scheme 3.10: Synthetic scheme for N,N,N',N'-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine (Series III)

Scheme 3.10 shows the synthetic route and structures of N,N,N',N'-tetrakis-(2-alkoxy naphthalen-1-yl)-benzene-1,4-diamine (Series III).

Table 3.5 gives the physical data of N,N,N',N'-tetrakis-(2-alkoxy-naphthalen-1-yl)-benzene-1,4-diamine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactant 1</th>
<th>Reactant 2</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>TENBD</td>
<td>B</td>
<td>M</td>
<td>95</td>
<td>48.57</td>
<td>20</td>
<td>Dark yellow crystals</td>
</tr>
<tr>
<td>TPNBD</td>
<td>C</td>
<td>N</td>
<td>85</td>
<td>44.65</td>
<td>22</td>
<td>Light brown needles</td>
</tr>
<tr>
<td>TBNBD</td>
<td>D</td>
<td>O</td>
<td>98</td>
<td>49.59</td>
<td>22</td>
<td>Brown needles</td>
</tr>
<tr>
<td>TPENBD</td>
<td>E</td>
<td>P</td>
<td>84</td>
<td>47.40</td>
<td>21</td>
<td>Brown needles</td>
</tr>
</tbody>
</table>
3.4.4. Synthesis of Series IV Compounds

3.4.4.1. Synthesis of N,N'-bis-(4-methoxyphenyl)benzene-1,4-diamine (Q)

1,4-Phenylene diamine (5.407 g, 0.05 mol), bromoanisole (12.50 ml, 0.1 mol), CuCl (0.0220 g, 0.0002 mol), 1.0 g of 1,10-phenanthroline and 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 20 ml of 1,2-dichlorobenzene for 16 hours at 170°C in oil bath under nitrogen atmosphere. Completion of the reaction was checked by TLC. The solvent was evaporated in vacuum and extracted using ether. It was washed with brine solution, dried over sodium bisulphite and concentrated to give a brown residue which was purified by column chromatography. It was recrystallized from ethanol.

Appearance: Brown solid, Yield- 65%, Melting point- 143°C.

Scheme 3.11 represents route and structures for the synthesis of N,N’-diphenyl benzene-1,4-diamine.

Scheme 3.11: Synthetic scheme for N, N’-diphenylbenzene-1, 4-diamine (Q).

3.4.4.2. Synthesis of N,N'-bis-(2-alkoxy-naphthalen-1-yl)-N,N'-bis-(4-methoxyphenyl)benzene-1,4-diamine (Series IV)
N,N'-Bis-(4-methoxy phenyl) benzene-1,4-diamine (Q) (16.01 g, 0.05 mol), Bromo alkoxy naphthalene (B-E) (0.1 mol), CuCl (0.0220g, 0.0002 mol), 1.0 g of 1,10-phenanthroline, 5.176 g of potassium carbonate (dried at 110°C) were refluxed together with 25 ml dichlorobenzene for 20 hours at 170°C in oil bath under nitrogen atmosphere. Completion of the reaction was checked by TLC.

After removal of the solvents under vacuum, ammonia solution (50 ml) was added and the mixture was left to stand for 2.0 hours. Ethyl acetate (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml × 2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, filtered and the solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate – hexane as eluent to obtain dark yellow solid which was recrystallized from ethanol-hexane mixture.

Scheme 3.12 represents route and structures for the synthesis of N,N'-Bis-(2-alkoxy-naphthalen-1-yl)-N,N'-bis-(4-methoxyphenyl)benzene -1,4-diamine (Series IV).
Scheme 3.12: Synthetic scheme for \(N,N'-\text{Bis-}(2\text{-alkoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine (Series IV)

Table 3.6: Physical data of \(N,N'-\text{Bis-}(2\text{-alkoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine (Series IV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactant</th>
<th>Melting point (°C)</th>
<th>Yield (%)</th>
<th>Reaction time (hrs)</th>
<th>Appearances</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENMBD</td>
<td>B</td>
<td>77</td>
<td>51.55</td>
<td>20</td>
<td>Dark yellow crystals</td>
</tr>
<tr>
<td>PNMBD</td>
<td>C</td>
<td>68</td>
<td>50.53</td>
<td>21</td>
<td>Yellow crystals</td>
</tr>
<tr>
<td>BMNBD</td>
<td>D</td>
<td>55</td>
<td>48.08</td>
<td>21</td>
<td>Yellow needles</td>
</tr>
<tr>
<td>PENMBD</td>
<td>E</td>
<td>76</td>
<td>49.00</td>
<td>22</td>
<td>Yellow crystals</td>
</tr>
</tbody>
</table>

**ENMBD**: \(N,N'-\text{Bis-}(2\text{-ethoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine, **PNMBD**: \(N,N'-\text{Bis-}(2\text{-propoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine, **BNMBD**: \(N,N'-\text{Bis-}(2\text{-butoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine, **PENMBD**: \(N,N'-\text{Bis-}(2\text{-pentoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine.

Table 3.6 gives the physical data of \(N,N'-\text{Bis-}(2\text{-alkoxy-naphthalen-1-yl})-N,N'\)-bis-(4-methoxy-phenyl) benzene-1,4-diamine (Series IV).

### 3.5. Instrumentation

Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8400 S spectrometer, where the percentage of transmittance versus wave number (in reciprocal of centimeters) was plotted. Solid samples were recorded as potassium bromide disc where as liquid samples as neat or as solvent spectra, using spectroscopic grade solvent.

Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu 1700 UV-Visible spectrophotometer using a closed type quartz tube of 1.0 cm square dimensions. All spectra were recorded at room temperature and
Experimental

at very low concentration of the solute. Spectroscopic grade ethanol, methanol and chloroform were used as solvent for UV spectra.

Emission spectra were recorded on PerkinElmer LS 45 Fluorescence Spectrometer using a closed type quartz tube of 1.0 cm square dimensions. Spectroscopic grade dichloromethane, ethanol, methanol and chloroform were used as solvent for UV spectra.

Proton (\(^1\)H) and carbon-13 (\(^{13}\)C) nuclear magnetic resonance (NMR) spectra were recorded on a NMR-JEOL GSX-400 spectrometer. The proton spectra were recorded using broad band inverse probe where the inner coil is for protons and outer coil for ‘X’ nuclei. Phase coherent solvent suppression was employed in some of the cases where the solvent signal is very strong compared to the sample signals. All the carbon-13 spectra were recorded in the dual (\(^{13}\)C/\(^1\)H) probe where the inner coil is for C-13 and the outer coil for protons. The decoupling of the proton was done employing waltz-16 sequence. The spectral parameters like number of scans, time domain data points etc were adjusted depending on the nature of the sample and the relaxation parameters like T1 and T2 were taken into account for obtaining the required information. The chemical shifts were reported in ppm unit with tetramethylsilane as internal standard. DMSO and CDCl\(_3\) were used as solvents.

Gas chromatography–mass spectrometry (GC-MS) analysis was carried out using a Varian 1200 L Single Quadrupole Gas Chromatograph-Mass Spectrometer. Helium is used as carrier gas. Column type used is WCOT fused silica Stationary phase – VF – 5MS with Column length 30m.

Electro chemical stability of the compounds was measured using Cyclic voltammetry (CV). CV measurements were carried out on a
Autolab potentiostat PGSTAT 12 at a glassy carbon electrode using millimolar solutions in acetonitrile (ACN) containing 0.1M of supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF$_6$), in a three electrode cell and potentiostat assembly at room temperature. The CV measurements were carried out at a glassy carbon electrode using millimolar solutions in acetonitrile containing 0.1M of the supporting electrolyte tetrabutylammonium hexafluorophosphate in a three electrode cell and potentiostat assembly at room temperature. The potentials were measured against platinum as reference electrode and each measurement was calibrated with an internal standard, ferrocene /ferrocenium (Fc) redox system.

Thermal characterization of the samples was determined using Differential Scanning Colorimetry (DSC). DSC studies were performed with a NETZSCH DSC 204 thermal analyzer under nitrogen atmosphere. The sample were scanned from -50°C to 150°C at the rate of 10°C min$^{-1}$. The compounds were analyzed for heating and cooling thermograms (cyclic) in nitrogen atmosphere from -50°C to 250°C at a rate of 10°C/ min. Glass transition ($T_g$), melting ($T_m$) and crystallization ($T_c$) were measured using DSC.