CHAPTER 2

Synthesis and characterization of
crown ether nano dyes
Resume

A series of novel crown ether based bis-diazo dyes were synthesized by the coupling of dibenzo-18-crown-6 bis-diazonium chloride with various compounds containing a phenolic group or an active methylene group. The compounds were purified and characterized by melting points, elemental analysis, FT-IR, $^1$H-NMR and FAB-MS. The particle sizes of the synthesized dyes were also determined by SEM and were found to be in the range of 20-25 nm.

A crown ether derivatized fulleropyrrolidine was also synthesized by the 1,3 dipolar cycloaddition between a crown ether based azomethine ylide and fullerene. The synthesized compound was purified and characterized by elemental analysis, FT-IR, $^1$H-NMR and MALDI-MS.
2.1 INTRODUCTION

Crown Ethers are macrocyclic polyethers whose structure contains hydrogen, carbon and oxygen atoms. The basic structure consists of oxygen atoms separated by organic spacers to give a conformation with a central cavity.

The exterior of the crown ether ring is hydrophobic while the interior is hydrophilic in nature. Hence, crown ethers possess the ability to complex ionic species or "guests" in the central cavity while the whole of the molecule can pass into a non-polar solvent (due to the hydrophobic exterior). Thus, crown ethers can acts as "hosts" taking ionic species as its "guest" [1].

Crown ethers were synthesized by Charles Pedersen, a chemist working at Du Pont when he was trying to prepare the multidentate ligand bis [2-(o-hydroxyphenoxy) ethyl] ether. Since then a large number of crown ethers and functionalized crown ethers have been synthesized and employed as phase transfer catalyst [2, 3], reagents for the determination and extraction of ions [4, 5], carriers for ion transport [6, 7] and as ion selective electrodes [8, 9].

There have been two synthetic approaches adopted for the synthesis of crown ethers and functionalized crown ethers. These are:

1. High dilution methods
2. Template directed methods

In high dilution methods, the reactants react in a large excess of solvent; this minimizes the chances of polymerization as well as the formation of by-products [10]. On the other hand, the template directed synthesis makes use of a template like a metal cation to increase the yield of the desired product [11]. The synthetic method adopted by Pedersen was a combination of the template directed
and high dilution methods (Fig. 1) [12]. These two methods are by far the most extensively used for the synthesis of various crown ethers [13, 14].

![Synthetic scheme for Dibenzo-18-crown-6](image)

**Fig. 1** Synthetic scheme for Dibenzo-18-crown-6

For further functionalization of the crown ether framework, simple condensation reactions [15], electrophilic substitutions [16], Mannich reaction [17], etc. have been adopted and various moieties such as the coumaryl [18], anthracyl [19], carboxylic acid [20], and amides [21] have been covalently linked to crown ethers to give analytically useful molecules [22]. If dyes/chromophores are combined with crown ethers, selective complexing agents that show visible color changes on complexation can be obtained. One of the earliest reports of such a molecule is by Vogtle and Dix wherein they had combined an azo dye with aza crown ether [23].

Later on not only the azo group but also other chromophores such as the picryl amino [24], nitro [25], styryl [26], butadienyl [27], naphthoquinone [28] etc were covalently linked to various crown ethers. However, the azo group remains the most versatile chromophore attached to crown ethers as they can be easily synthesized and gives bright as well as highly intense colors. The crown dyes were prepared by a slow precipitation method to reduce the particle size. Further, a “Top Down” approach was adopted to obtain dye particles in nanometer sizes.
Secondly, fullerene crown conjugates are also attracting considerable attention because of their interesting redox properties [29-31]. Most of these conjugates are known to complex alkali and alkaline earth metal ions [32-34]. So far, there are no reports on complexation of crown fullerene derivatives with transition metal ions. Hence, the introduction of complexing moieties such as Schiff base is desirable on crown fullerene conjugates to achieve novel complexing ligands for transition metal ions.

Considering both the above views in the present investigation, two different substituted crown ethers have been synthesized:

1. Crown ether azo dyes
2. Crown Schiff base fullerenopyrrolidine

The synthesis of the crown ether azo dyes involved the following steps:

2. Nitration of Dibenzo-18-crown-6
3. Reduction of cis-dinitro dibenzo-18-crown-6
4. Diazotization of cis-diamino dibenzo-18-crown-6
5. Coupling of dibenzo-18-crown-6 diazonium chloride with various couplers

Various substituted naphthols, pyrazolones, acetoacetanilides and barbituric acid were chosen as couplers for the present work. These coupling components are easily available and are known to give highly stable and brightly colored dyes [35]. The synthesized compounds were purified and characterized by melting points, elemental analysis, FT-IR, $^1$H-NMR and FAB-MS.

Fullerene was derivatized with dibenzo-18-crown-6 using a cycloaddition reaction between a crown-ether based azomethine ylide and fullerenes. The synthesis of the crown Schiff base fullerenopyrrolidine involved the following steps:
1 Synthesis of Dibenzo-18-crown-6
2 Nitration of Dibenzo-18-crown-6
3 Reduction of cis-dinitro dibenzo-18-crown-6
4 Schiff base condensation of cis-diamino dibenzo-18-crown-6 with terephthaldehyde
5 1,3 dipolar cycloaddition of the crown ether based azomethine ylide with the fullerene

2.2 EXPERIMENTAL

2.2.1 Instrumentation

Melting points were determined on a Toshniwal (India) melting point apparatus and are uncorrected. Elemental analysis was done on a Heraeus Carlo Erba-1108 analyzer. FT-IR spectra were recorded on a JASCO-410 FT-IR spectrophotometer as KBr pellets. Visible spectra were recorded on a Hitachi U-3210 UV-visible spectrophotometer, and the FAB mass spectra were recorded on a JEOL SX-102 / DA - 6000 mass spectrometer / data system using argon / xenon (6KV, 10mA) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. m-Nitro benzyl alcohol (NBA) was used as the matrix and the matrix peaks appeared at m/z 136, 137, 154, 289, 307. $^1$H NMR spectra were recorded on a DRX-300 spectrophotometer operating at 300 MHz in DMSO-d$_6$ with TMS as the internal standard.

The MALDI TOF MS were run on a Micromass Tof Spec 2E instrument using a nitrogen 337 nm laser (4 ns pulse). At least 40-50 shots were summed up. The matrix used is 2, 5-dihydroxy benzoic acid dissolved in chloroform and the
matrix was spotted on MALDI target and allowed to dry before introducing into the mass spectrometer.

Scanning Electron Microscope measurements were carried out on a Leo Electron Microscope, U.K., Model No. 440I. The dyes were dispersed in double distilled deionized water using a sonicator. The samples were then mounted onto a stainless steel sample plate and coated with gold using plasma. The samples thus prepared were then studied using SEM.

2.2.2 Chemicals and Reagents

Compounds 3-hydroxy-N-phenyl-2-naphthamide 3a, 3-methyl-1-phenyl-pyrazole-5-one 4a, acetoacetanilide 5a and corresponding derivatives (3b-3f, 4b-4d, 5b-5d) were obtained as gift samples from Trident Colors, Ahmedabad and were purified before use. Barbituric acid 6 was purchased from Loba Chemie and used without purification.

Fullerene and sarcosine were obtained from Aldrich while terephthaldehyde was obtained from Fluka. All other chemicals and solvents used were of analytical grade and were used without further purification.

2.2.3 Synthesis of crown ether bis-diazo dyes

The synthesis of dibenzo 18-crown-6, nitration to cis 4, 4'-dinitrodibenzo-18-crown-6 and reduction to cis 4, 4'-diaminodibenzo-18-crown-6 was carried out by reported procedures [12, 36, 37] (Fig. 1,2 & 3). 4, 4'-diaminodibenzo-18-crown-6 was diazotized by the conventional procedure to obtain the crown ether bis-diazonium chloride 2 [38] which was then coupled with 3a-3f, 4a-4d, 5a-5d and 6 using reported methods [35].
**Chapter 2/synthesis and characterization**

Dibenzo-18-crown-6 →

![Synthetic scheme for cis 4, 4'-dinitro dibenzo-18-crown-6](image)

**Fig. 2** Synthetic scheme for cis 4, 4'-dinitro dibenzo-18-crown-6

Cis 4, 4'-dinitro dibenzo-18-crown-6

Cis 4, 4'-diamino dibenzo-18-crown-6

**Fig. 3** Synthetic scheme for cis 4, 4'-diaminodibenzo-18-crown-6
2.2.3.1 Synthesis of 4, 4'-bis-diazonium dibenzo-18-crown-6 chloride 2

4, 4'-diaminodibenzo-18-crown-6 (5.0 g, 0.013 mol) was dissolved in concentrated hydrochloric acid (15 ml) and the solution was then cooled to 0-5 °C. Sodium nitrite (2.0 g, 0.029 mol) in water (10 ml) was then added to this solution drop wise with vigorous stirring, for 1 h at 0-5 °C. The excess of nitrous acid was destroyed using sulphamic acid until the solution was negative to starch iodide paper (Fig. 4). The bis-diazonium chloride thus obtained used directly for coupling without isolation.

![Cis 4, 4' diamino dibenzo-18-crown-6](image1) ![4, 4' bis-diazonium dibenzo-18-crown-6 chloride](image2)

**Fig. 4** Synthetic scheme for 4, 4’ bis-diazonium dibenzo-18-crown-6 chloride

2.2.3.2 Synthesis of 3-hydroxy-N-phenyl-2-naphthamide based crown dyes 7a-7f

The compound (3a-3f) (0.034 mol) was dissolved in 200 ml of 0.2 M sodium hydroxide solution and heated slowly to 90° C. The resulting clear solution was then cooled to room temperature and a dilute solution of acetic acid was introduced drop wise into the above solution until a fine dispersion of the coupler was obtained. This suspension was then cooled to 0° C and the diazotized solution was slowly added with stirring. A pH of 6-7 was maintained during the reaction using sodium acetate. Stirring was continued for about 3-4 h at 0° C and then the solution was gently heated to 90° C. The precipitated dye (7a-7f) was filtered and recrystallized in methanol (Fig. 5 and Table 1).
**Chapter 2/synthesis and characterization**

4, 4’ bis-diazoium dibenzo-18-crown-6 chloride 2

![Chemical structure diagram](image)

$pH = 6-7$

3a-3f

7a-7f

**Fig. 5 Synthetic scheme for dyes 7a-7f**
Table 1 The various substituents and colors obtained for dyes 7a-7f

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<thead>
<tr>
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<th>R₁</th>
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<tr>
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<td><img src="image.png" alt="Image" /></td>
<td>f</td>
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</tbody>
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2.2.3.3 Synthesis of 3-methyl-1-phenyl-pyrazole-5-one and barbituric acid based crown dyes 8a-8d and 10

The coupler (4a-4d and 6) (0.034 mol) was dissolved in 100 ml water containing sodium hydroxide (3 g, 0.075 mol) and 5 gm of sodium acetate. The solution was cooled to 0°C and the diazonium solution was added slowly. The pH during the reaction was maintained between 9-12. The stirring was continued for 4-6 h and then heated to boiling. The dye (8a-8d and 10) was collected by filtration and recrystallized in methanol. (Fig. 6 & 7 and Table 2)
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4, 4' bis-diazonium dibenzo-18-crown-6 chloride 2

Fig. 6 Synthetic scheme for dyes 8a-8d

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Table 2 The various substituents and colors obtained for dyes 8a-8d

<table>
<thead>
<tr>
<th>R₂</th>
<th>Color</th>
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<td>c</td>
<td><img src="c.png" alt="image" /></td>
<td>d</td>
</tr>
</tbody>
</table>

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2.2.3.4 Synthesis of acetoacetanilide based crown dyes 9a-9c

The diazo solution was neutralized with sodium acetate to the point where Congo red paper just turned violet. The compound (5a-5d) (0.034 mol) was dissolved in 50 ml water containing sodium hydroxide (1.36 g, 0.034 mol) to form a clear solution. This solution was cooled and 7 g of sodium acetate was added. Dilute acetic acid was then slowly added until a faintly acid reaction to litmus was produced but taking care that no precipitation occurs. The diazo solution was then added and the reaction continued for 10 h. The dye was collected by filtration. (Fig 8 and Table 3)
Fig. 8 Synthetic scheme for dyes 9a-9d

Table 3 The various substituents and colors obtained for dyes 9a-9d

<table>
<thead>
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<td>b</td>
<td>![Image of color]</td>
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<td>c</td>
<td>![Image of color]</td>
<td>![Image of color]</td>
</tr>
<tr>
<td>d</td>
<td>![Image of color]</td>
<td>![Image of color]</td>
</tr>
</tbody>
</table>
2.2.4 Particle size of the dyes

The dyes were prepared by a slow precipitation method i.e. the dyes were dissolved in basic solutions and then reprecipitated by slow neutralization using acid under vigorous stirring. Further, a top down approach was adopted to obtain the dye particles in nanometer sizes. Hence, the dyes were milled in a Spex ball mill for ten minutes at 1080 rpm and were obtained in very small particle sizes which was determined using SEM.

2.2.5 Synthesis of crown ether based fulleropyrrolidine

The synthesis of dibenzo 18-crown-6, nitration to 4, 4'-dinitrodibenzo-18-crown-6 and reduction to 4, 4'-diaminodibenzo-18-crown-6 was carried out by reported procedures [12, 36, 37] (Fig. 1, 2 & 3).

2.2.5.1 Synthesis of crown ether based dialdehyde 11

A solution of 4, 4'-diaminodibenzo-18-crown-6 (5 mmol, 2 g) in chloroform was added dropwise to a refluxing solution of terephthaldehyde (10 mmol, 1.34 g) in chloroform during a period of 6 h. The resulting mixture was then subjected to column chromatography (silica gel, eluent toluene/methanol, 8:2). The dialdehyde obtained was isolated and recrystallized from hexane/chloroform, 4:6. (Fig. 9)

2.2.5.2 Synthesis of crown ether based fulleropyrrolidine 12

A mixture of 72 mg (0.1 mmol) of C60, 18 mg (0.2 mmol) of N-methylglycine, and 31 mg (0.5 mmol) of 11 was refluxed in 60 mL of toluene under argon for 10 h. The resulting brown solution was concentrated under vacuum and subjected to column chromatography (silica gel, eluent toluene: ethyl
acetate, 3:1). The product obtained was recrystallized from methanol/dichloromethane(3:7) to give 12 as a mixture of conformers. (Fig. 10)

Fig. 9 Synthetic scheme for crown ether based dialdehyde 11

Fig. 9 Synthetic scheme for crown ether based dialdehyde 11
Fig. 10 Synthetic scheme for crown ether based fulleropyrrolidine 12
2.3 RESULTS AND DISCUSSION

2.3.1 Crown ether bis-diazo dyes

Fifteen novel crown dyes (7a-10) were synthesized from 4, 4'-diaminodibenzo-18-crown-6. The yields as well as the color of the synthesized dyes were found to be highly dependent on the pH of the reaction. Hence, the pH was very carefully maintained during the reaction.

2.3.1.1 Physical properties

The physical properties of the dyes are given in Table 4. The dyes showed colors ranging from deep red (\(\lambda_{\text{max}}\) 546 nm) to yellow (\(\lambda_{\text{max}}\) 384 nm). The dyes were found to be soluble in almost all organic solvents viz. ethanol, toluene, ethyl acetate, chloroform, N, N' dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) but completely insoluble in water.

2.3.1.2 Infrared Spectra

The appearance of the azo band at 1514-1610 cm\(^{-1}\) confirms that all the dyes contain the azo group in the solid state while the appearance of the \(-\text{OH}\) bands at a much lower value 3450-3472 cm\(^{-1}\) for dyes 7a-7f, 8a-8d and 9a-9d indicates the presence of strong intramolecular hydrogen bonding. The hydroxyl groups in these dyes are in close proximity to the diazo group or a carbonyl group hence can easily form hydrogen bonding. The presence of three carbonyl bands and the absence of the \(-\text{OH}\) band in the FT-IR spectra of dye 10 suggest that it is in the azo-triketo form in the solid state.

The presence of the secondary amide group in 7a-7f was confirmed by the observation of the \(-\text{NH}\) stretching between 3250-3230 cm\(^{-1}\) and \(-\text{C}=\text{O}\) stretching
between 1641-1621 cm\(^{-1}\). The \(-\text{NH}\) stretching is also seen in 9a-9d between 3240-3235 cm\(^{-1}\) while in case of 10 it is observed at 3244 cm\(^{-1}\) (Table 5).

2.3.1.3 \(^1\)H NMR Spectra

The \(^1\)H NMR spectra of the fifteen newly synthesized crown ether bis-diazo dyes is given in Table 5.

The \(-\text{OH}\) and \(-\text{NH}\) peaks observed in the \(^1\)H NMR were very broad and diminished in nature. In fact the enolic \(-\text{OH}\) proton peak for dyes 8a-8d and \(-\text{NH}\) for dye 10 (observed in the FT-IR) were not at all observed in the NMR spectra.

2.3.1.4 Mass spectra

The FAB-mass spectral data of the newly synthesized dyes is given in Table 4.

2.3.2 Particle size

The SEM measurements show the particle sizes of the dyes to be in the range of 20-25 nm (Table 4). Hence, crown ether nano dyes have been successfully prepared by the mechanical milling method. The SEM photographs of the dyes 7a, 8a, 9a and 10 are shown in Fig 11-14. The photograph shows that the dyes are all in the form of flaky crystals. Since all the dyes have particle sizes, less than the visible light wavelength they will scatter the light effectively giving extremely bright colors.
Table 4 Physical properties of the crown ether dyes 7a-10

<table>
<thead>
<tr>
<th>Dye</th>
<th>Molecular formula</th>
<th>FAB-Mass (M+l)</th>
<th>λ_max (nm)</th>
<th>Particle size (nm)</th>
<th>% Yield</th>
<th>%C Calc.</th>
<th>%C Found</th>
<th>%H Calc.</th>
<th>%H Found</th>
<th>%N Calc.</th>
<th>%N Found</th>
<th>Melting point (Decom. Temp)°C</th>
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<tbody>
<tr>
<td>7a</td>
<td>C₅₄H₄₆N₆O₁₀</td>
<td>939</td>
<td>528</td>
<td>20-25</td>
<td>86</td>
<td>69.07</td>
<td>69.01</td>
<td>4.94</td>
<td>4.72</td>
<td>8.95</td>
<td>8.85</td>
<td>178 (&gt;200)</td>
</tr>
<tr>
<td>7b</td>
<td>C₅₆H₅₈N₆O₁₂</td>
<td>983</td>
<td>536</td>
<td>20-25</td>
<td>86</td>
<td>68.43</td>
<td>68.01</td>
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<td>5.32</td>
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<td>8.75</td>
<td>175 (&gt;200)</td>
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<td>967</td>
<td>530</td>
<td>20-25</td>
<td>87</td>
<td>69.55</td>
<td>69.77</td>
<td>5.21</td>
<td>5.33</td>
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<td>180 (&gt;200)</td>
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<td>7d</td>
<td>C₅₄H₄₄N₄O₁₄</td>
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<td>527</td>
<td>20-25</td>
<td>82</td>
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<td>4.69</td>
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<td>546</td>
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<td>87</td>
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<td>407</td>
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<td>62.65</td>
<td>62.10</td>
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<td>5.02</td>
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Table 5. Spectral data for the synthesized dyes 7a-10

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Chapter 2/synthesis and characterization
Fig. 11 SEM image for dye 7a

Fig. 12 SEM image for dye 8a
Fig. 13 SEM image for dye 9a

Fig. 14 SEM image for dye 10
2.3.3 Crown ether based fulleropyrrolidine

The synthesis of the crown ether based dialdehyde 11 was achieved by the slow addition of 4, 4'-diaminodibenzo-18-crown-6 to the solution of terephthaldehyde, which reduced the possibility of polymerization and byproduct formation. The bis functionalization of C$_{60}$ using the dibenzo-18-crown-6 tether was achieved by Prato’s fulleropyrrolidine synthetic methodology [39]. The dialdehyde 11 reacts with sarcosine to give an azomethine ylide which further reacts with the (6, 6) bond in fullerene via a 1, 3 dipolar cycloaddition reaction to give the crown ether fulleropyrrolidine.

2.3.3.1 Physical properties

The physical properties of the synthesized compounds are given in Table 6. The synthesized compound 12 was found to be soluble in organic solvents like chloroform, dichloromethane, and toluene but insoluble in water.

2.3.3.2 Infrared Spectra

The infrared spectral data for 11 and 12 is given in Table 7. The presence of bands at 1711 cm$^{-1}$ (C=O) and 1643 cm$^{-1}$ (C=N) in the FT-IR spectra confirmed the presence of the formyl group and the Schiff base linkage in compound 11.

2.3.3.3 $^1$H NMR Spectra

The presence of the two proton peak at 9.87 ppm (-CHO) and at 8.51 ppm (CH=N-) in the $^1$H-NMR confirms the presence of the formyl group and the Schiff base linkage in compound 11 (Table 7). The $^1$H-NMR of the compound 12 shows four different –CH$_3$ peaks between 0.95 to 1.87 ppm, which clearly indicates that it exists in different isomeric forms [40]. These isomers were not separated and hence the studies reported further are the average values of these geometric isomers.
2.3.3.5 Mass spectra

The FAB-mass spectral data of the newly synthesized dyes is given in Table 6.

Table 6 Physical properties of compound 11 and 12

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Molecular formula</th>
<th>Mass</th>
<th>% Yield</th>
<th>%C (Calc.</th>
<th>Found</th>
<th>%H (Calc.</th>
<th>Found</th>
<th>%N (Calc.</th>
<th>Found</th>
<th>Melting point (°C)</th>
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<tr>
<td>11</td>
<td>C_{36}H_{34}N_{2}O_{8}</td>
<td>623 (M+1)</td>
<td>30</td>
<td>69.4</td>
<td>69.9</td>
<td>5.46</td>
<td>5.68</td>
<td>4.5</td>
<td>4.12</td>
<td>168</td>
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<tr>
<td>12</td>
<td>C_{100}H_{44}N_{4}O_{6}</td>
<td>1419(M+23)</td>
<td>13</td>
<td>85.9</td>
<td>85.6</td>
<td>3.15</td>
<td>3.04</td>
<td>4.0</td>
<td>3.96</td>
<td>&gt;300</td>
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</table>

Table 7 Spectral data of compound 11 and 12

<table>
<thead>
<tr>
<th>Comp</th>
<th>IR (cm⁻¹)</th>
<th>¹H NMR (δ, ppm)</th>
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<tbody>
<tr>
<td></td>
<td>ν_C=N</td>
<td>ν_C=O -OCH₂ Ar-H -CHO -N=CH</td>
</tr>
<tr>
<td>11</td>
<td>1711 1634</td>
<td>3.3-4.5 6.94-8.1 9.87 8.51</td>
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<tr>
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<td>(16H, m)</td>
<td>(10H, m) (2H, b) (2H, b)</td>
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<tr>
<td>12</td>
<td>1667</td>
<td>3.5-4.2 6.9-8.0 8.43</td>
</tr>
<tr>
<td></td>
<td>(16H, m)</td>
<td>(10H, m) (2H, b)</td>
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</tbody>
</table>
2.4 CONCLUSION

The newly synthesized crown ether azo dyes were well characterized and had intense as well as bright hues. The dyes had particle sizes in the range of 20-25 nm and were soluble in almost all organic solvents.

The synthesized crown dyes have been used as colorants for flexographic and gravure inks which is discussed in Chapter III. They have also been studied as colorants for inkjet inks using a microemulsion technique. The performance as well as durability of the inks formulated and the colorants therein have been thoroughly studied which is discussed in Chapter IV.

The novel crown Schiff base fulleropyrrolidine combines the complexing abilities of both the crown ether cavity and the Schiff base linkage. Hence, it has been studied for its complexing properties with alkali and alkaline earth metal ions and with copper ions. The changes in the redox behavior of the fullerene moiety with metal complexation has also been studied which is discussed in Chapter V.
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