Unsaturated 15 and 16 Membered Appended Naphthalene Macrocyclic Molecules for The Development of Fluorometric Chemosensors

S Hasan, S Salleh, S Hamdan, and B Yamin

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

e-mail:sharizal187@perlis.uitm.edu.my

Abstract. Unsaturated macrocyclic molecules have got an interest due to their potential in catalysis, ion exchange and electron transfer. Salicaldehyde derivatives macrocyclic molecules have a broad range in synthesis. In this study, two unsaturated macrocyclic molecules (L1 and L2) have been synthesized. The preparation of unsaturated macrocyclic ligands involve two steps; the reaction of salicylaldehyde with 1,2-dibromoethane or 1,4-dibromobutane to produce precursor, then cyclisation were completed using Schiff base technique by adding diamines (naphthalene diamine). The ligands were characterized spectroscopically. In FT-IR spectrums, the form of the ligands mainly can be observed on the disappearance of the carbonyl group of aldehyde at approximately 1650 cm\(^{-1}\) that was readily assigned to C=O group of salicylaldehyde with the replacement of C=N peak at 1684.13 cm\(^{-1}\). The success in producing macrocyclic ligands have been further characterized using fluorescence emission spectroscopy (FES) and revealed the typical emission of naphthalene at \(~430\text{ nm}\). Fluorescence changes of L1 and L2 showed high selectivity for Fe\(^{3+}\) and Cu\(^{2+}\) respectively in the presence of other common metal ions, such as Zn\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\). Besides, the ligand was sensitive enough to detect the concentration of ferric ion with the detection limit down to 1.08 \(\times\) 10\(^{-6}\) M and fluorescence change that was unaffected by the presence of other common coexisting metal ions. Complexation with Co(II) was also attempted.

Keywords: Macrocyclic Schiff base, Macrocyclic complexes, 1,2-bis(2-carboxyaldehyde phenoxy)ethane, Cobalt(II) complexes, 1,8- Naphthalenediamine, Fluorophore.
1. Introduction

The macrocycles are important as a strong ligand in coordination with transition metal in coordination of chemistry. Macrocyclic ligand consist of different donor atoms that attached to the central ions and appended with an aromatic ring. Nitrogen, phosphorus, sulphur and oxygen is a donor atoms that is important in the coordination of the ligand with the metal ion [1]. The differences of donor atoms will give different force of bonding and different strength. Meanwhile, appended aromatic ring will delocalize the electron and result more efficient interactions between the molecules and the complex because of the molecule contain the π bond along the ring of the molecules.

Fluorophore is a chemical compound that able to re-emit light upon light excitation. Generally, it consists of aromatic groups or cyclic molecules. It can bind with the ligand to form selective and sensitive sensors in biological, clinical, and environmental interest. The investigation using fluorophore intrigued many researchers due to its low cost, easily performed, high sensitivity and versatility in typical of photoluminescence spectroscopy [2]. The fluorophore is able to send a signal in the responses of the selectivity of the metal. It combines with the ligand to form macrocyclic complexes. Among various fluorophore, 1,8-naphthalenendiamine is one of the useful tools due high stoke shift [3]&[4], which makes it appropriate for constructing macrocyclic complexes. Metal complexes have advantageous photophysical properties, such as high stability and relatively long lifetimes compared with those of organic fluorophores. Therefore, 1,8-naphthalenendiamine was chosen as a fluorophore due to their excellent photophysical properties, high fluorescence quantum yield and good coordination ability. Herein, we report a convenient and efficient route for the preparation of macrocyclic ligand by using Schiff base technique. It exhibits the stronger of fluorescence, so the molecule is more rigid and stable.

The purpose of this research is to construct 15 and 16 membered appended naphthalene macrocyclic complexes denoted as a macrocyclic ligand by using schiff base technique. In this research, schiff base is formed by reaction of salicylaldehyde and diamine derivatives because this reaction mostly form stable complexes with the transition metals. The interactions between the Co(II) complexes with N-donor ligands that containing binding units suitable for coordination of single metal ion. In addition, schiff base also capable of acting to as multidentate ligands for coordination with transition metal ions [5]. This technique has been known to form C=N in which will increase the stability of complex form by coordination of N with the metal and the electron will be delocalized among the three atoms (C, N and metal).

2. Experimental

2.1. Instruments

Elemental analysis was carried out on a Thermo Finnigan Flash EA 110 Elemental Analyzer. 1H Infrared spectra were obtained on Perkin Elmer Spectrum 100 FT-IR 1750X FTIR spectrophotometer on KBr discs in the range 4000–600 cm⁻¹. Fluorescence excitation and emission spectra were recorded on a Luminescence Spectrometer LS 55 using 1 cm pathlength cuvettes at room temperature. The excitation and emission slit widths were 15 nm. 5 x 10⁻⁵ M solution of the sensor L1 and L2 in CH3OH: H2O (9:1), Tris-HNO3= 10 mM, pH=7 and 1 x 10⁻³ M solutions of the cations were prepared respectively. Fluorescence titrations were carried out by the incremental addition of 40 μL– 400 μL guest solutions to 3ml of sensor L1 and L2 in the cuvette respectively. The receptors and cation solutions were prepared as 5 x 10⁻⁵ M in CH3OH:H2O (9:1), Tris-HNO3= 10 mM, pH=7.0 for Job’s plot.

2.2. Materials

The salicylaldehyde derivatives used in the synthesis were prepared from salicylaldehyde, 1,2-dibromoethane or 1,3-dibromopropane and K₂CO₃ as shown in Scheme 1 and according to the literature method [6] and [7]. All the other chemicals and solvents were of analytical grade and used as received.
Scheme 1. Synthesis of 1,3-bis(2-carboxyaldehyde phenoxy)propane

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2.3. Synthesis of Schiff Base

Cautiously, diamine (5mmol) in methanol (40mL) was added drop wise to a stir solution of salicylaldehyde derivatives (1.5g, 5mmol) in methanol (60mL). Then, the reaction was reflux for 48 hours at 100°C. After the addition had completed, the reaction was left at room temperature for several hours and continued filter and wash with cool methanol and dried in the air. Figure 1 shows the step in synthesis of macrocyclic ligands, L1a and L2b

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\text{Figure 1. Step in synthesis of macrocyclic ligands, L1a and L2b}
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2.4. Synthesis of complexes

To a homogeneous ligand, Co(II)chloride-6-hydrate (1.85g, 5mmol) in methanol(60mL) was added dropwise to the macrocyclic of 1,2-bis(2-carboxylaldehydehydephenoxy)ethane (1.5g, 5mmol) in 40mL methanol. While stirring the mixture was reflux for 3-4 hours at 60°C. Then, the precipitate was filtered and washed with cool methanol dried to the air. The step in synthesis of macrocyclic complexes, L1a1 and L2b2 are shown in Figure 2.
2.5. Association constant calculation
Generally, for the formation of 1:1 complexation species formed by the receptor and the guest cation, the following Benesi–Hildebrand equation was used to determining the association constants (Ka).

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\frac{1}{(F - F_0)} = \frac{1}{(F_a - F_0)} + \frac{1}{K(F_a - F_0)} \times \frac{1}{[M^{n+}]}
\]

Where F, F0 and Fa are the emission intensities, respectively in the absence and infinite concentration of the metal ion (Mn⁺) [8]. Fa is the fluorescence intensity in the presence of excess amount of Mⁿ⁺. Therefore, for 1:1 complex formation, the double reciprocal plot of 1/(F – F0) against 1/[Mⁿ⁺] should give a straight line; from the slope and intercept of which, the equilibrium constant (K) can be calculated.

3. Result and discussion
3.1. Infrared Spectroscopy (FT-IR) of Macrocyclic ligands, L1a and L2b
The macrocyclic ligand L1a and L2b formations were obtained from the condensation of the carbonyl compound in methanol as a solvent with 1:1 mole ratio as stated in step in synthesis of macrocyclic ligands, L1a and L2b reaction in methodology. The macrocyclic result on FT-IR of L1a and L2b are shown in the figure 1.1a. There is one main feature in the infrared spectrum of the macrocyclic compound. The first one is disappearance of the characteristic (C=O) group at that has been replaced with (C=N) peak. This band range is shown in Table 1.
As shown in Table, the range of (C=N) peak for the L1a and L2b macrocyclic is between 1633\,cm^{-1} to 1638\,cm^{-1} which was has lower wave number from the disappearance peak of (C=O). According to the research done by (Ilhan, 2007) found that the (C=N) peak shifted towards to lower energy region due to the coordination of nitrogen in the compound. Besides, due to the appearance of nitrogen in the compound IR spectra on (C-O-C) peak showed a different between a free ligand and the macrocyclic which the bands of (C-O-C) has shifted towards to lower wave number with high energy level. Peak for the L1a macrocyclic that exist at 1633.25\,cm^{-1} compared to the free ligand that exists at 1290.44 \,cm^{-1}. This phenomenon explained by research done by (Ilhan, 2007), the (C-O-C) bands has undergone stretching vibrations due to the conformational changes in the compound.

**Table 1:** FT-IR data for ligand L1a and L2b

| Interpretation | Macroyclic compound | Peak frequency (cm^{-1}) |
|----------------|---------------------|--------------------------|
| C=N L1a        |                     | 1633.25                  |
| C=N L2b        |                     | 1638.52                  |

**Figure 3a.** FT-IR result on L1a macrocyclic compound

**Figure 3b.** FT-IR result on L2b macrocyclic compound
3.2. Infrared Spectroscopy (FT-IR) of Macrocyclic complexes, L1a1 and L2b2
For the L1a1 complexes the cobalt peak has appeared at 3224.15 cm\(^{-1}\). The peak has shifted to a lower wavenumber region which means lower energy. According to (Ebrahimi, 2014) the peak for complexes has shifted towards lower wavenumber side due to the coordination of the complexes to the metal ions through the lone pair of electrons on the nitrogen. In addition the peak of (C-O-C) band explained by research done by (Ilhan, 2007) has appeared at 1286.37 cm\(^{-1}\) also has shifted to the lower wave number region because of the involvement of metal to the macrocyclic compound. The result on IR spectrum of L1a1 is shown in figure 3.c. The IR spectrum on the L2b2 macrocyclic complexes also has shown a medium broad peak as L1a1 macrocyclic complexes at 3225.25 cm\(^{-1}\). This peak also has shifted to the left to the lower wave number side. This phenomenon has been explained by (Ebrahimi, 2014) on his research that this phenomenon happens due to the lone pair of nitrogen as mentioned above.

![FT-IR of macrocyclic complex, L1a1.](image)

3.3 Elemental analyzer of Macrocyclic
Elemental analyzer test has been done on the macrocyclic compound since the macrocyclic compound exists in the form of solid. From the experimental composition and the values on C, H and N of the macrocyclic compound it can be said that Schiff base technique to produce macrocyclic compound are acceptable. From the table 4 the experiment data on the total percent error can be said that for the ligand L1a and L2b the percent composition is between 86 to 87% that is 86.164% and 87.261% respectively. The result is acceptable for the formation of the macrocyclic. The experimental ratio that acquired for C:H and C:N also close to the theoretical ratio that confirmed the formation of the macrocyclic.

| Compound     | Theoretical ratio (%) | Experimental ratio (%) | Total error (%) | Total composition (%) |
|--------------|-----------------------|------------------------|----------------|----------------------|
| C\(_26\)H\(_{30}\)N\(_2\)O\(_2\), L1a | 26:2.0 26:20 | 26.1:2.0 17.83:29.0 | 9.379 | 86.184 |
| C\(_{27}\)H\(_{32}\)N\(_2\)O\(_2\), L2b | 27:2.0 27:22 | 21.8:2.5 25.7:21.4 | 6.911 | 87.261 |
3.3. Fluorescence spectroscopic studies

Selectivity is an important characteristic of an ion-selective chemosensor. To investigate the selectivity of L1 and L2 the fluorescence selectivity experiments of various metal Fe$^{3+}$, Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ were studied. The emission spectra of L1 and L2 after the addition of different metal cations in CH$_3$OH:H$_2$O are shown in Fig.4(a and b).

![Fluorescence spectra of L1 (a) and L2 (b), in CH$_3$OH:H$_2$O](image)

Based on the result of fluorescence spectra, upon addition of 5.0 x 10$^{-3}$ M each of metal ions in CH$_3$OH:H$_2$O there are significant change on the fluorescence spectra of L1 and L2 were observed. The emission intensity of L1 increased significantly after addition of 5.0 x 10$^{-3}$ M Fe$^{3+}$ ion. Meanwhile for the L2, there is a change in emission intensity after addition of 5.0 x 10$^{-3}$ M Fe$^{3+}$ and Cu$^{2+}$. Change in emission intensity of sensors L1 and L2 were considered after addition of Fe$^{3+}$ ion and Cu$^{2+}$ ion is due to the formation of stable complex due high stoke shift, which makes it appropriate for constructing macrocyclic complexes. As it is revealed from selectivity studies above the response of sensors toward Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ were the same, but Fe$^{3+}$ and Cu$^{2+}$ showed different response. The emission intensity of sensors of Fe$^{3+}$ and Cu$^{2+}$ was lower than the other metal ions. Thus Fe$^{3+}$ and Cu$^{2+}$ were selected to study the fluorescence response profiles and detection limit. It exhibit the stronger of fluoroscence, so the molecule is more rigid and stable.
Further studies on sensitivity of compounds L1 and L2 were conducted on selected metal. As shown in Fig. 5a, 5b and Fig 6a, 6b the sensitivity studies of fluorescence intensities were performed using 5.0 x 10^{-5} M solution of L1 and L2 in CH_3OH:H_2O with different concentration of Fe^{3+} for L1 and Cu^{2+} for L2.

The results showed that the emission intensity was linearly changed with increasing ferric ion concentration for L1 and copper ion concentration for L2. To determine the detection limit, the relative fluorescence intensity was plotted as a function of Fe^{3+} and Cu^{2+} concentration, the detection limit was calculated based on the fluorescence titration. The numerical value of limit of detection is calculated using 3 Sb/m [9], where Sb is standard deviations of the blank and m is slope the calibration curve. The limit of detection L1 and L2 are 1.08x10^{-6} M and 1.2025x10^{-7} M respectively. According to the state regulations, the concentration of the iron ions in the sewage discharge is not more than 1.79x10^{-6} M [10].

3.4. Job plot study
To determine the binding stoichiometry of L1 and Fe^{3+}, Job's method for absorbance measurement was carried out. Keeping the sum of the initial concentration of L1 and Fe^{3+}, the molar ratio of Fe^{3+} was varied from 0 to 1. As shown in Fig.7a, the fluorescence reached a maximum when the ratio of [Fe^{3+}]/([Fe^{3+}]+[L1]) was 0.5, indicating 1:1 stoichiometry of Fe^{3+} to L1 in the complex. From the fluorescence titration profile (Fig.7b), the binding constant (K_a) of L1 with Fe^{3+} ion was calculated according to the 1:1 model (2.9 x 10^{5} M). According to the Fig. 8a and 8b, the result for the L2 and
Cu$^{2+}$ also shows the same ratio and stoichiometry to the L1 and the binding constant (Ka) of L2 with Cu$^{2+}$ ion was calculated according to the 1:1 model ($1.37 \times 10^6$ M). These values were accepted because in the range of those ($10^3 - 10^5$ M) which previously reported for binding chemosensor The high value of association constant Ka indicates that strong complex formation takes place between L1 and Fe$^{3+}$ ion.

Figure 7a. Job plot of a 1:1 complex of L1 and Fe$^{3+}$, where the intensity was plotted against the mole fraction of Fe$^{3+}$. The total concentration of Fe$^{3+}$ with receptor L1 was $10 \times 10^{-5}$ M.

Figure 7b. Benesi-Hildebrand plot of L1 ($5 \times 10^{-5}$ M) based on 1:1 binding stoichiometry.

Figure 8a. Job plot of a 1:1 complex of L2 and Cu$^{2+}$, where the intensity was plotted against the mole fraction of Cu$^{2+}$. The total concentration of Cu$^{2+}$ with receptor L2 was $10 \times 10^{-5}$ M.
4. Conclusion

In this study, the macrocyclic ligands have been synthesis successfully by Schiff base technique. The formation of macrocyclic ligands have been proved by the FT-IR spectrum with the appearance of C=N in the range 1633 cm\(^{-1}\) to 1638 cm\(^{-1}\). Elemental analyzer confirmed the theoretical and experimental value suggesting the attachment of diamine derivatives into the aldehyde precursor to form the macrocyclic. Fluorescence changes of L1 and L2 showed high selectivity for Fe\(^{3+}\) and Cu\(^{2+}\) respectively in the presence of other common metal ions, such as Zn\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\). Besides, the ligand was sensitive enough to detect the concentration of ferric ion and copper ion with the detection limit down to 1.08 x 10\(^{-6}\) M and 1.2025 x 10\(^{-7}\) M respectively. However, the presence of other common coexisting metal ions especially cobalt ion which is used for the analysis of the complex were unaffected to the fluorescence change due to the low stoke shift and low of stability to form macroyclic complex.

5. References

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