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Ionic Liquid Based Fluorescent Sensors for Cations

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IONIC LIQUID BASED FLUORESCENT SENSORS FOR CATIONS

By

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ABSTRACT

The development of novel fluorescent sensors for cations is an area of current interest. Most of these sensors are large organic molecules that have a low solubility in water and are not suitable to be used as sensors in water. The goal of this study is to develop a new sensor by attaching an ionic liquid group to make it water-soluble. We have used a well-known photoinduced electron transfer (PET) sensor for protons as our first test. This sensor is based on a chromophore-spacer-receptor design that is based on an anthracene chromophore and a morpholine proton receptor. The sensor is non-fluorescent at high pH due to PET between the tertiary nitrogen atom of the receptor and the chromophore. The PET can be quenched by protonation of the nitrogen atom leading to a fluorescent signal at low pH. As this sensor is not water-soluble all fluorescence studies have been carried out in methanol water mixtures. In this study, we have attached a methyl imidazolium group to the anthracene to make this sensor a water-soluble ionic liquid. The new sensor was prepared by selectively functionalizing the 9 and 10 positions of an anthracene and the fluorescence studies of the new ionic liquid based sensor were carried out in water.

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Firstly, I would like to extend my gratitude to my research advisor, Dr. de Silva. Thank you for your continuous guidance and patience throughout the duration of this project. I would also like to thank Dr. Isidor for inviting us to collaborate on this project and for his guidance and assistance throughout the project. In addition, I would like to thank Dr. Olsen for helping me with the instruments and Dr. Konas for reviewing this thesis. Lastly, I would like to thank my family for all of their love and support.

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INTRODUCTION

Fluorecent Photoinduced Electron Transfer Sensors

Sensing of cations such as protons and s-block metals such as Ca^{2+}, Li^+, and Na^+ is very important in chemistry and biology. Over the past few decades many sensors based on the photoinduced electron transfer (PET) process have been developed for cellular imaging of these cations.[1,2,3] These sensors have a chromophore-spacer-receptor design which can be seen in Figure 1.[4] The chromophore, also called the fluorophore, is usually a highly fluorescent molecule, such as anthracene that is responsible for emitting a fluorescent signal. The receptor is the component responsible for the recognition and binding of the target cation. Tertiary amines are often used as receptors in PET sensors. The final component is an akyl spacer that links the chromophore to the receptor. The spacer is used to maintain the chemical independence of the chromophore and receptor. However, it should be short enough so that the election transfer can take place. A commonly used spacer is a methylene group.
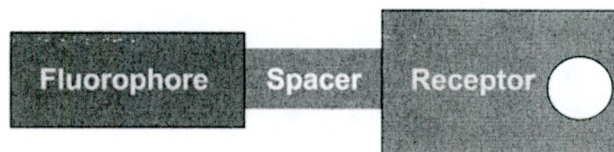

Figure 1: PET sensor Fluorophore-Spacer-Receptor design.[4]

PET sensors can behave as an "Off-On" or an "On-Off" switch with cation binding. The principle behind an "Off-On" PET sensor is that when the chromophore

absorbs a photon and there is no analyte bound to the receptor, there is a transfer of an electron from the receptor to the chromophore. This transfer then blocks the relaxation of the chromophore electron and therefore blocks the emission of the fluorescent signal. Conversely, when there is an analyte bound to the receptor, the electron transfer process is hindered and the chromophore electron can relax back to its ground state emitting the fluorescent signal as it releases the energy.

From a molecular orbital stand point, in the "Off" state, the highest occupied molecular orbital (HOMO) of the free receptor is higher in energy than that of the chromophore. Upon excitation of the chromophore, there is an electron transfer from the HOMO of the chromophore to its lowest unoccupied molecular orbital (LUMO). This leaves a vacancy in the HOMO of the chromophore which is filled by the photoinduced electron transfer from the receptor to the chromophore. The excited chromophore electron cannot relax back down thus, fluorescence is not emitted. This process can be seen in Scheme 1 (A).
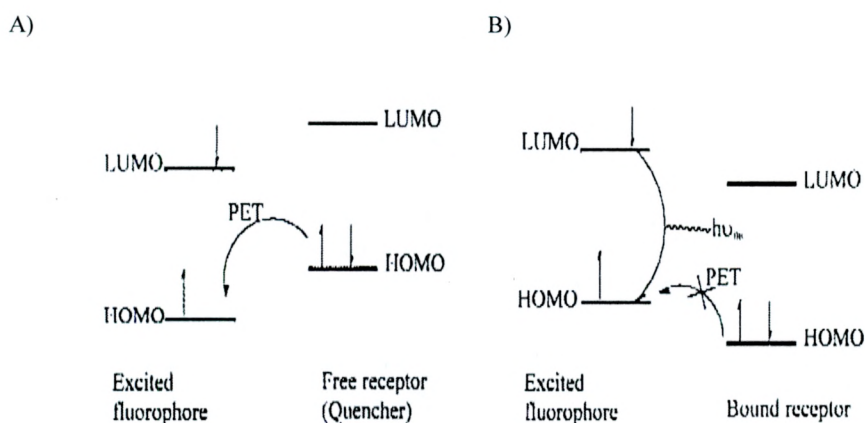
Scheme 1: Molecular Orbital energy diagram of the PET process. A) "Off" state of the sensor; B) "On" state of the sensor.

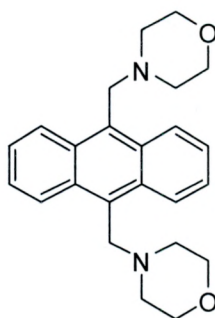Once the receptor binds a cation, the sensor switches to its "On" state. In terms of molecular orbitals, the HOMO of the receptor is now at a lower energy than that of the chromophore. This blocks the PET from the receptor to the chromophore. Now, the excited electron from the chromophore can relax back to its ground state, releasing the extra energy as fluorescence. See Scheme 1 (B).

The PET process can be explained from a thermodynamics perspective by the application of the modified Weller equation.[5]

$$\Delta G_{et} = -E_s + E_{ox.donor} - E_{red.\ acceptor}$$

The terms E_s, $E_{ox.donor}$, and $E_{red.\ acceptor}$ represent the singlet energy, oxidation potential of the donor (cation receptor) and the reduction potential of the acceptor (chromphore), respectively. When ΔG_{et}, the free energy of electron transfer, is less than zero, the transfer is thermodynamically favorable. In an "Off-On" sensor, when the cation binds the oxidation potential of the receptor ($E_{ox.donor}$) increases. This then makes ΔG_{et} a positive number and the electron transfer is thus unfavorable and fluorescence occurs.

DND-167 (**1**) is an example of a commercially available "Off-On" PET sensor used for protons.[6] It consists of an anthracene backbone with two morpholine moieties as receptors. At high pH the sensor is non-fluorescent due to the electron transfer from the tertiary amine in the morpholine to the anthracene. However, at lower pH the sensor becomes fluorescent due to the protonation of the tertiary amine which hinders the electron transfer.

1

The second type of PET sensor has an "On-Off" switch with cation binding. These sensors emit fluorescence when there is no analyte bound to the receptor. Once the cation binds to the receptor, a PET process occurs and fluorescence is quenched. In these sensors, in the "On" state, the LUMO of the receptor is higher in energy than the chromophore energy levels. Therefore, the PET process is unfavorable and the relaxation of the excited chromophore electron emits fluorescence. This process is seen in Scheme 2(A). Once the cation binds, the LUMO of the receptor becomes lower in energy than the LUMO of the chromophore. The excited electron from the chromophore transfers to the LUMO of the receptor, hindering its relaxation back to the ground state and quenching the fluorescent emission (Scheme 2(B)).

A)   B)
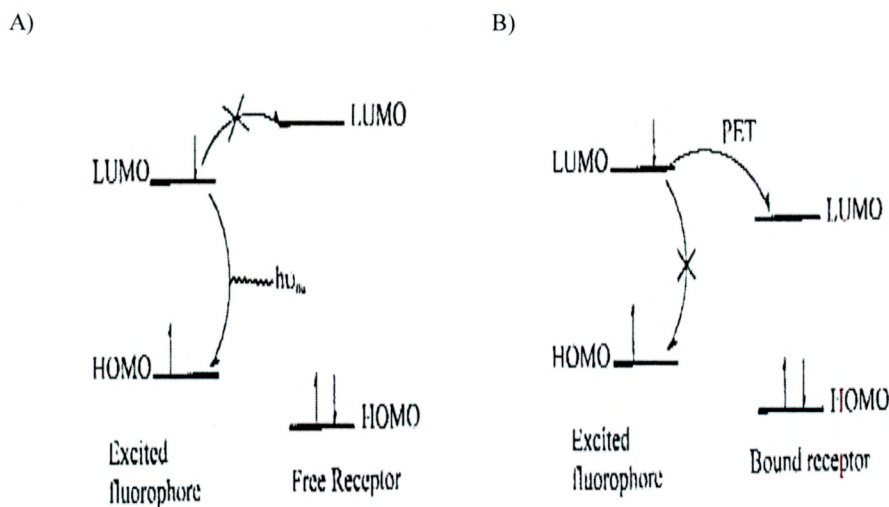
Scheme 2: Molecular Orbital energy diagram of the PET process. A) "On" state of the sensor; B) "Off" state of the sensor.

In terms of the Weller equation, when the cation binds to the receptor, the reduction potential of the acceptor (cation receptor) increases. This leads to a more negative ΔG_{et} and the electron transfer becomes thermodynamically favorable leading to fluorescence quenching. Sensor **2** is an example of an "On-Off" switch.[7] At high pH the sensor is fluorescent but becomes non-fluorescent when the pyridine ring is protonated at low pH.
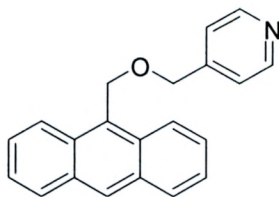
2

Ionic Liquids

Ionic liquids are molten salts that are known to have low melting points. Over the past couple of decades the term has been used specifically for those salts which have a melting point lower than 100°C, even though salts with higher melting points still fall into the traditional category of ionic liquids. Within the modern category of ionic liquids are a special group of ionic liquids which have received much attention in research. These are known as room-temperature ionic liquids because they have melting points at or below 25 °C, which makes them liquids at ambient temperatures. The first ionic liquid discovered was Ethanolammonium nitrate in 1888. Since then, interest in these compounds has grown tremendously because they have a wide range of unique physical and chemical properties that allow for their applications in various disciplines within the chemical field.[8,9]
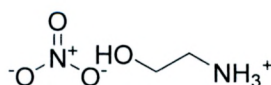
Figure 2: The first ionic liquid discovered, Ethanolammonium nitrate [8].

Ionic liquids are salts that are comprised of organic cations with organic or inorganic anions. Although there are many possible cations, the most commonly used cations are: akylammonium, diakylimidazolium, or N-akylpyridinium. Likewise, there many anions to choose from but, the most commonly used include: halides (Cl^- and Br^-), nitrate, hexaflourophosphate, and tetrafluoroborate. Other anions that can be used include: chloroaluminates, akyl sulfates, and tosylate.[8]The commonly used cations and

anions can be seen in Figure 3. The availability of different cation-anion combination leads to a plethora of possible ionic liquids. For example, the combination of 50 cations with 30 anions leads to a formation of 1500 different ionic liquids.[10]

A)
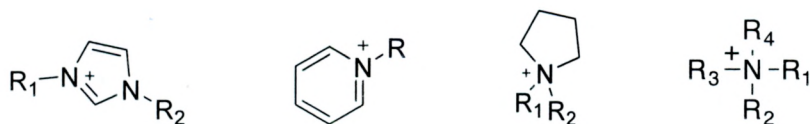
B)

Figure 3: Commonly used: A) cations and B) anions in the synthesis of ionic liquids.

There are various methods for synthesizing ionic liquids. One of the most frequently used methods is through the alkylation of the nucleophilic cation precursor with a haloalkane.[11] This method is readily used for the production of imidazolium based ionic liquids. These ionic liquids can also be used as the starting material for the formation of different ionic liquids. For example, anion exchange can be done to change the halogen counter ion with one such as [NTf$_2$]$^-$. In recent years it has been shown that diakylimidazolium halides ionic liquids can also be prepared in a microwave without any solvent or the need for excess amounts of the akyl halide.[8]

Ionic liquids have many different physical and chemical properties which brings them considerable attention in research.[9] One of the intriguing properties of these compounds is that they have melting points over a large range of temperatures. The melting temperatures vary depending on the cation and anions used. It has been found that larger anions decrease the melting temperature. For example, 1-ethyl-3-methylimidazolium chloride has a smaller anion than 1-ethyl-3-methylimidazoliumttetrachloroaluminate and has a higher melting point; 87°C vs. 7°C, respectively.[8] In the same manner, larger cations with longer akyl side chains have lower melting points. In other words, the physical state in which an ionic liquid will be found at ambient temperature depends on how well the ions can pack together and form a crystalline structure.

Another unique feature of ionic liquids is that they can be made to be either hydrophilic or hydrophobic. The miscibility of particular ionic liquids with water is determined by how well the ions can coordinate with the water molecules. In particular, the anion component of the ionic liquids has been found to have the dominating influence on the solubility of the ionic liquid in water.[10] Therefore, as the coordinating ability of the anion increases, the hydrophilicity of the ionic liquid increases. For example, an ionic liquid with an anion of hexafluorophospahte is hydrophobic while having the same cation with a chloride anion will make the ionic liquid more hydrophilic. The nature of the cation can have some effect on the solubility but, this effect is not as significant as that of the anion.

Ionic liquids are also known to have low vapor pressures, large liquidus range, and high thermal decomposition temperatures. A low vapor pressure means that these

compounds are not likely to evaporate and pose a risk to neither the environment nor health. The latter two mentioned properties allow them to be used solvents in reactions requiring high temperatures without suffering degradation. Therefore, ionic liquids are considered ideal candidates for the replacement of traditional volatile organic solvents.

The list of unique properties of ionic liquids is not limited to those mentioned above. Other properties exploited include: viscosity, density, heat capacity, ability dissolve organic and inorganic materials, conductivity, and electrochemical potential window. Due to these qualities and the ability to fine tune these properties through the manipulation of the cation and anion combinations ionic liquids can be used in a wide range of applications. These can include: catalysis, extraction, gas handling, reaction solvents, and many more.[9]

In regards to the optical properties of ionic liquids, there have been conflicting findings. At the center of the studies for the fluorescent nature of ionic liquids have been those based on the imidazoliumcation. It was first concluded that these ionic liquids did not have any significant emission in the visible or UV range. Furthermore, any absorption in these regions was attributed to impurities in the ionic liquid.[12] However, optical studies conducted on three purified ionic liquids: 1-Butyl-3-methylimidazolium hexafluorophosphate, 1-Butyl-3-methylimidazolium tetrafluoroborate, and 1Ethyl-3-methylimidazolium tetrafluoroborate found that there is non-negligible absorption in all of the UV region and a tail that extends into the visible range. These compounds can be seen in Figure 4.
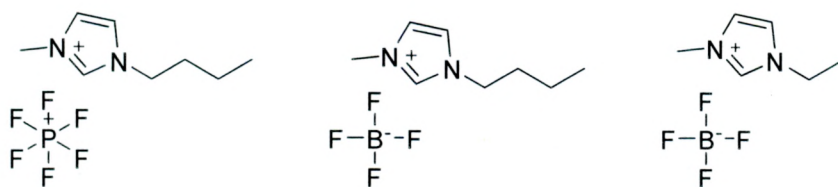
Figure 4: Ionic liquids whose optical properties show non-negligible absoprtion. 1-Butyl-3-methylimidazoliumhexafluorophosphate, 1-Butyl-3-methylimidazolium tetrafluoroborate, and 1Ethyl-3-methylimidazolium tetrafluoroborate respectively.

These compounds have been found to have weak fluorescence and the fluorescence quantum yieldswere found to be between 0.005 and 0.02 when excited at 360nm. It has been shown that symmetrically substituted ionic liquid such as 1,3-butylimidazolium chloride, Figure 5, have stronger fluorescence spectra.[13] This particular ionic liquid was found to be highly fluorescent and the fluorescence was quenched by the addition of hemoglobin to the ionic liquid. This addition results in the coordination of the iron from the heme group with the imidazoliumcation, making the molecule unsymmetrical. Hence, the fluorescent nature has been attributed to the symmetry of the molecule.
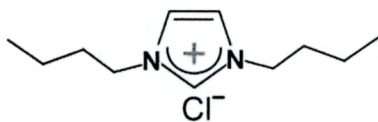

Figure 5: 1,3-butylimidazolium chloride.

<div align="center">GOAL</div>

The main goal of this thesis was to synthesize *1-methyl-3-((10-morpholinomethyl)anthracen-9-yl)methyl)-1H-imidazol-3-ium chloride* (**10**). This is a PET sensor with an "Off-On" switch which is activated by the protonation of the tertiary amine on the morpholine receptor at low pH values. In addition, the sensor has an imidazolium based ionic liquid moiety which makes the sensor water soluble. Secondly, we wanted to study how the fluorescence of this molecule compares to molecules of similar structure.
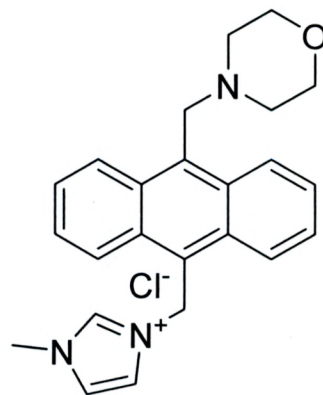
1-methyl-3-((10-(morpholinomethyl)anthracen-9-yl)methyl)-1H-imidazol-3-ium chloride

RESULTS AND DISCUSSION

Synthesis of sensor **10**

The synthesis of sensor **10** has been previously attempted using 9,10-bis(chloromethyl)anthracene with the goal of attaching a morpholine at one position and then a methyl imidazole at the other position. While this method produced a small amount of the desired product, this is not a good method as it is difficult to control the selective substitution of each chloromethyl group. This is mainly due to the very low solubility of the 9,10-bis(chloromethyl)anthracene in many common organic solvents.

In our approach, we used the commercially available starting material, 9-methylanthracene-10-carboxaldehyde (**5**). We have also prepared this compound in the lab by the Wolff-Kishner reduction of 9-anthracenecarboxaldehyde (**3**) followed by the Vilsmeier-Haack reaction to functionalize the 10 position with an aldehyde group. The detailed synthesis is described in the experimental section.

The 9 and 10 positions of **5** were successfully functionalized in a series of steps which are summarized in Scheme 3. Firstly, the methyl group was brominated with NBS. The product can be identified in ^{1}HNMR spectrum by the aldehyde signal at 11.50 ppm and the methylene signal at 5.51ppm. The bromo compound, **6**, was then aminated with morpholine to yield compound **7**. The ^{1}HNMR shows two new signals at 3.66 and 2.64 ppm corresponding to the four hydrogens of the morpholine adjacent to the oxygen and nitrogen, respectively.

After the successful attachment of the morpholine receptor at the 10 position, the remaining synthesis steps were performed selectively at the 9 position. Firstly, the

aldehyde was reduced by refluxing with $NaBH_4$. Both the ^1HNMR and the $^{13}CNMR$ spectra lack the aldehyde signal, confirming the formation of the alcohol product **8**. In addition, the signal for the methylene group adjacent to the alcohol can be seen at 5.69 ppm in the ^1HNMR.

The next step was the chlorination of the alcohol. Initially, this was done by refluxing in toluene with thionyl chloride for 90 minutes. This gave a brown solid in 72% yield. Subsequently, milder chlorination conditions were employed. The reaction was performed in dichloromethane and stirred at room temperature for 30 minutes, yielding product **9** in 85%. The ^1HNMR shows the shift in the methylene group from 5.69 to 5.65 ppm as the chlorine replaces the alcohol. The change in the $^{13}CNMR$ is more evident as the shift changes from 57.55 to 39.29 ppm.

Lastly, compound **9** was refluxed with 1-methyl imidazole in toluene for one hour. After refluxing, and removing the solvent of the rotary evaporator, the product was isolated as a gummy brown solid. This was then washed with diethyl ether to remove excess methyl imidazole leading to a powdery brown solid. The ^1HNMR shows a signal at 10.98 ppm which corresponds to the hydrogen between the two nitrogen atoms in the imidazole ring.
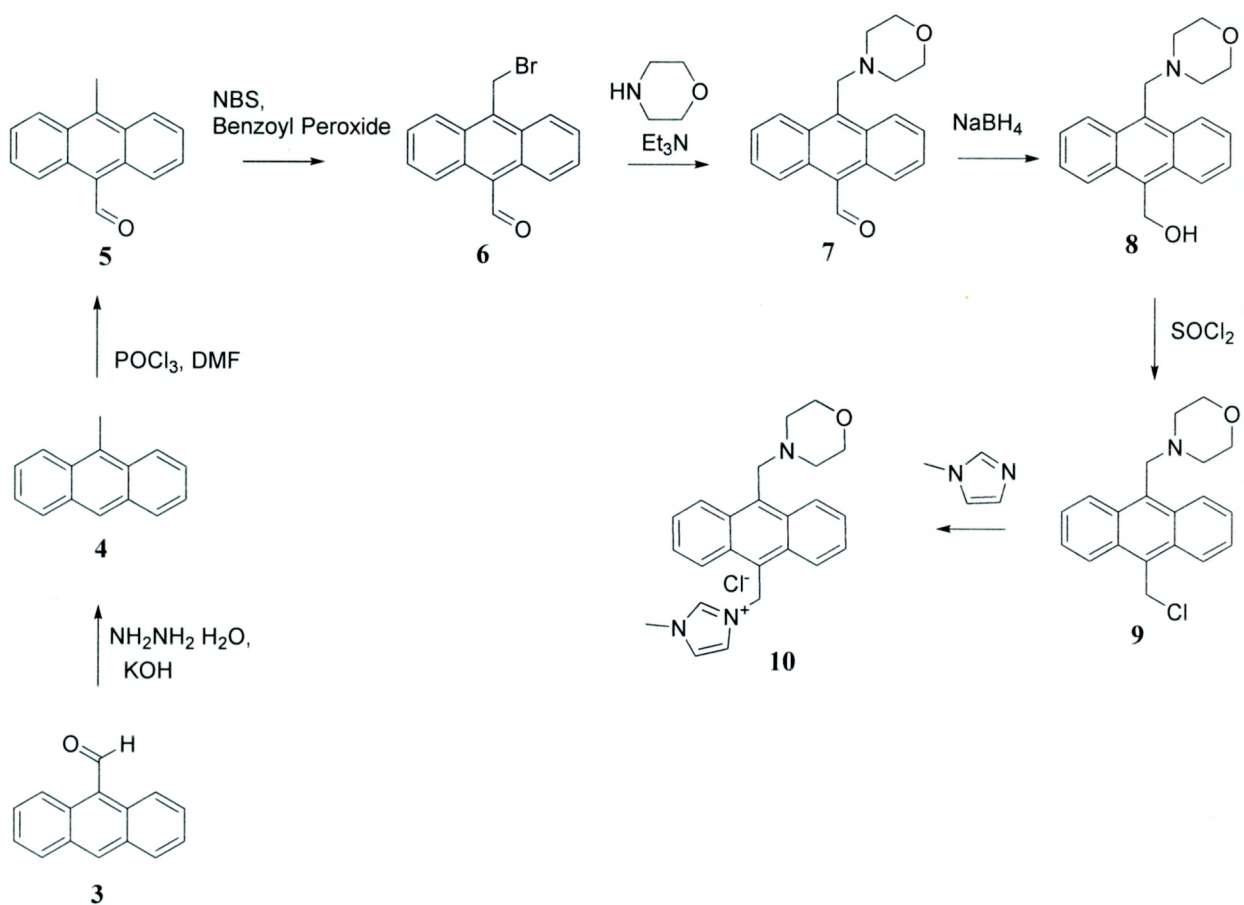
Scheme 3: Synthesis of Ionic Liquid PET sensor **10**.

Further purification of the compound was attempted by recrystallizing **10** in

acetonitrile. After 3 days, as the acetonitrile evaporated and fine, yellow crystals were

formed. When the ¹HNMR was obtained however, it did not match that of the crude

product. Specifically, the shift corresponding to the hydrogen between the nitrogen atoms

on the imidazole ring was no longer present. When the NMR spectrum of the crystals was

compared to the chloro compound, **9**, the spectra were identical. This could mean that

attempts to recrystallize in acetonitrile have lead to the cleavage the methyl imidazole

moiety with a nucleophilic attack of the chloride. Further investigation is needed to

confirm this as could also mean that there was some unreacted starting material that
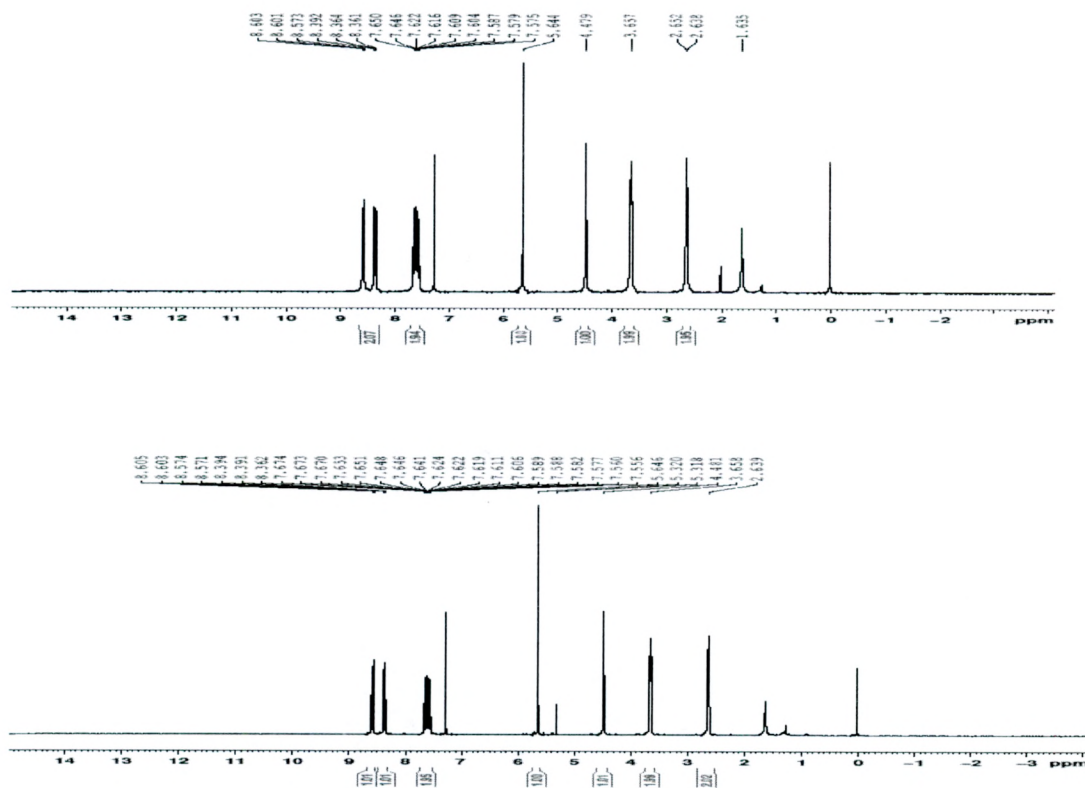
crystallized in acetonitrile.

Figure 6: A comparison of NMR data for compound **9** (top) and **10** after recrystallization

in acetonitrile (bottom)

Mass spectrometry was also used to confirm the target mass and hence the

formation of the ionic liquid. We dissolved 5 mg Sensor **10** in 20 mL of 50:50

methanol:water mixture and ran it through the LC-MS. The mass of the ionic liquid

expected was 372.4 g/mol. The mass detected however, was 290.3 g/mol. The difference

in mass corresponds to the methyl imidazole moiety, suggesting the cleavage of the

methyl imidazole. To confirm the cleavage pattern of the ionic liquid, we ran the mass

spec of compound **11**. Again, there was a mass difference of 82.1 g/mol between the found and expected masses, 191.25 vs. 273.35 g/mol respectively. The mass spectra of the compounds are seen in Figure 7 and the cleavage mechanisms can be seen in Scheme 4.
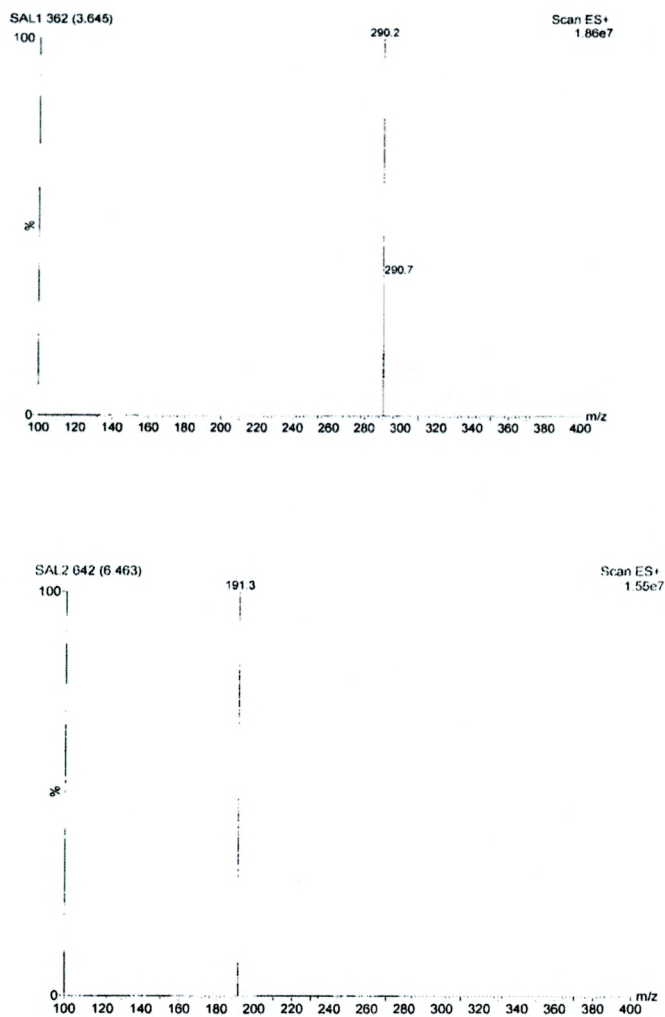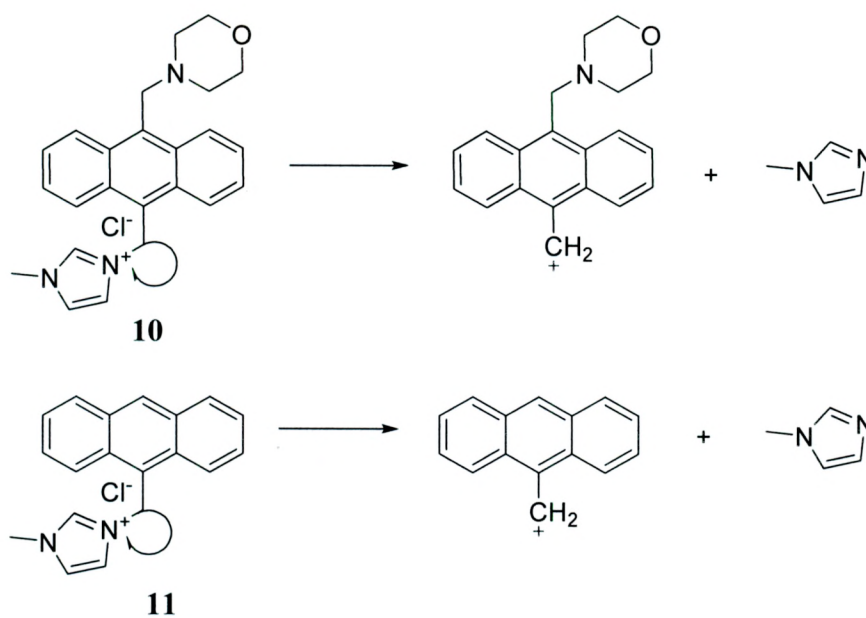

Figure 7: Mass spectrum of sensors **10** (top) and **11** (bottom) in 50:50 methanol:water.

Scheme 4: LC-MS (50:50 methanol:water) cleavage mechanism of compound **10** and **11**.

Water Solubility of Ionic Liquid Sensor **10**

The ionic liquid sensor **10** was designed as a hydrophilic ionic liquid by using a chlorine anion. In contrast, the precursor **9** is not hydrophilic. To test the change in hydrophilicity, 10 mg of each, **9** and **10**, was dissolved in 20 mL of water. As expected, there was a marked increase in the water solubility which can be seen in Figure 8.
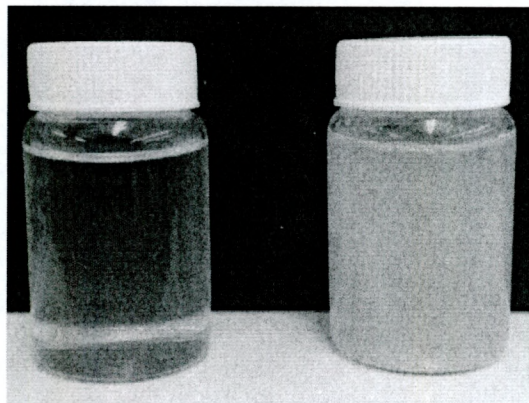

Figure 8: Comparison of the increase in water solubility of compound **10** vs. compound **9** (10 mg in 20 mL of H_2O).

Fluorescent Studies of Sensor **10**

Sensor **10** has an anthracene as a chromophore and a morpholine that acts as the receptor and switch of the sensor. At high pH, it is in the "off" state because the PET process between the receptor and chromophore is thermodynamically favored. As the pH is lowered, the tertiary amine of the morpholine is protonated and the PET process is hindered. Hindrance of the PET allows the sensor to become fluorescent. Figure 9. shows the change in fluorescent intensity as the pH decreases when hydrochloric acid is added to the sensor dissolved in water.
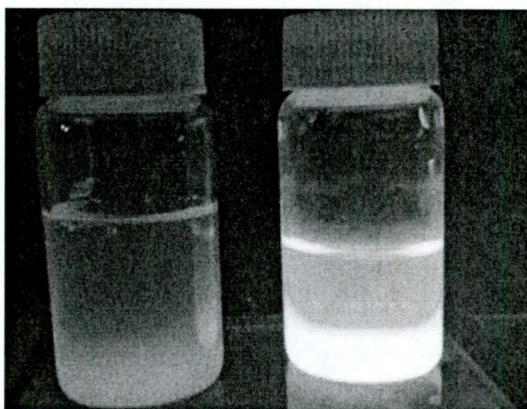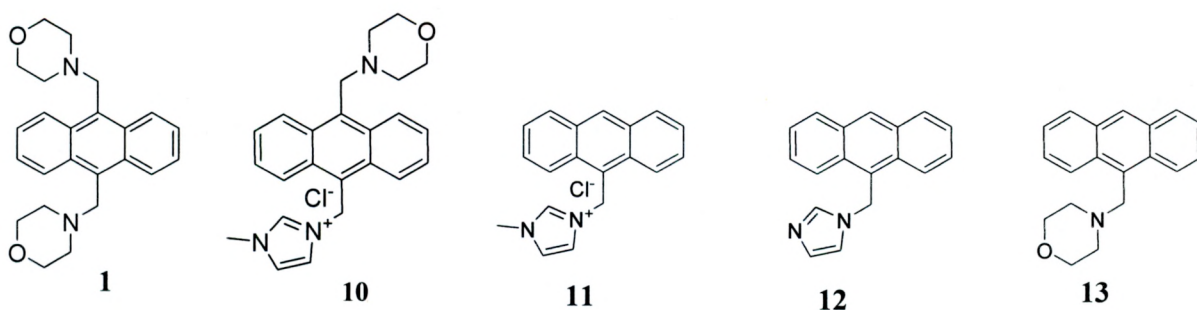

Figure 9: Increase in fluorescence of compound **10** in water at high pH (left) and low pH (right).

Fluorescence studies of **10** show that the imidazolium group does not have a significant effect on the PET process of the sensor. The fluorescence of **10** was also compared with **1, 11, 12 & 13**.

The intensity of fluorescence as a function of pH for compounds **1, 10, 12 & 13** are shown in Figure 10. For compound **10** there is negligible fluorescence emitted at high pH. As the pH decreases, the intensity increases indicating the trigger of the "Off-On" switch of the sensor. The intensity then reaches a maximum at pH 2, which corresponds to the complete protonation of the receptor. The same trend is seen for compounds **1** and **13**, indicating that the ionic liquid moiety does not significantly affect the fluorescence of the sensor. In contrast, the emission of compound **12** is not completely quenched. This observation is consistent with what is reported in the literature indicating that the PET process is not as efficient as our sensor **10**. The lone pair of the nitrogen in **12** is delocalized in the imidazole and is not fully available for PET, which leads to the partial quenching of fluorescence of **12** at high pH.
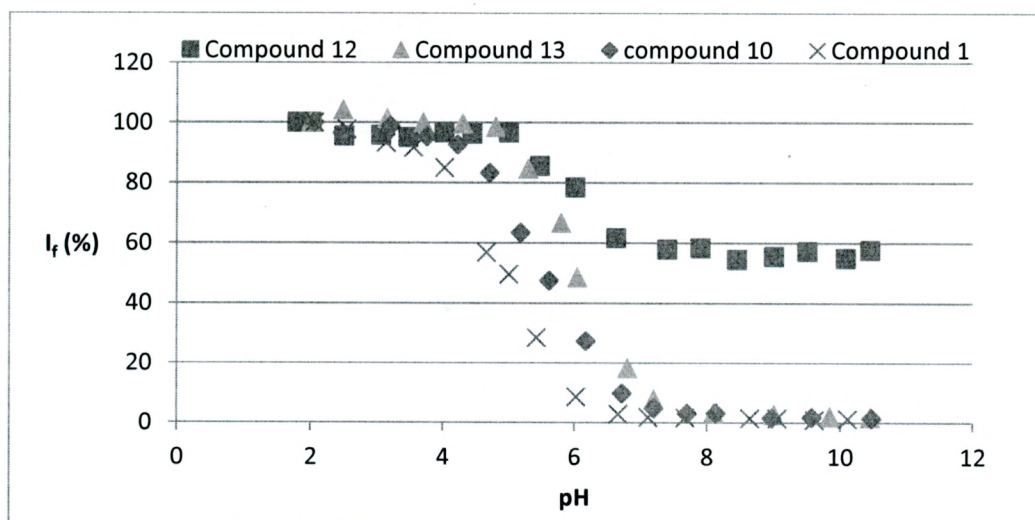
Figure 10: I_f dependence on pH of compounds **1**, **10**, **12** and **13** in 50/50 MeOH/H$_2$O. (λ_{ex}= 350 nm, λ_{em}= 370-550 nm). pH was adjusted by adding HCl or NaOH.
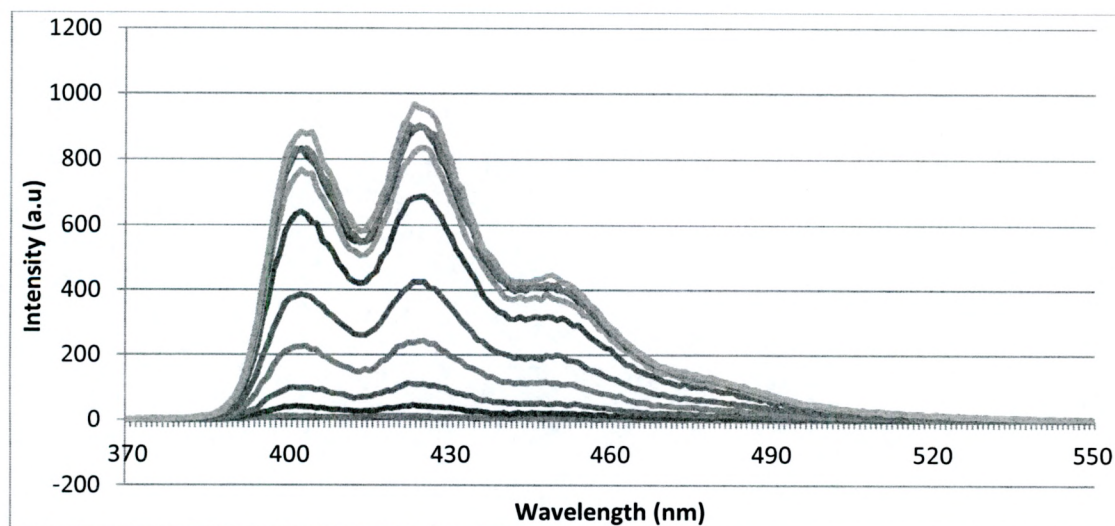

Figure 11: Fluorescence emission spectra of sensor **10** (10^{-5} M in water). (λ_{ex}= 350 nm, λ_{em}= 370-550 nm). Highest intensity= pH 2; lowest intensity= pH 10.20. pH was adjusted by adding HCl or NaOH.

The fluorescence quantum yields were measured by comparing the area of the fluorescence spectrum of each compound with the area of the fluorescence spectrum of 9,10-diphenylanthracene in solutions that have the same concentration. The fluorescence quantum yield data is summarized in Table 1.

Quantum Yield Data

Compound	Solvent	pH	Φ_f
1	50:50 MeOH	2	0.80
		10	0.01
10	100% H_2O	2	0.85
		10	0.01
10	50:50 MeOH:H_2O	2	0.89
		10	0.02
	100% MeOH	N/A	0.74
11	50:50 MeOH:H_2O	N/A	1.09
	100% H_2O	N/A	1.21
12	50:50 MeOH: H_2O	2.04	0.75
		10.08	0.46
13	50:50 MeOH: H_2O	2.15	0.99
		10.20	0.03

Table 1: Quantum yield data for compounds 10, 11, 12, 13, 14, and 15. 9, 10-diphenylanthracene was used as a reference for calculating quantum yields. (λ_{ex}= 350 nm, λ_{em}= 370-550 nm.).

The fluorescence quantum yields for the sensor **10** in 100 % H_2O at pH 2 and 10 are 0.85 and 0.01, respectively. We were interested in comparing the fluorescence of sensor **10** with compounds **1**, **11**, **12** and **13**. Since most of these compounds are not water soluble the measurements were made in 50:50 MeOH: H_2O. The fluorescence quantum yield for **1** is comparable of the literature value. However, the values for **11** and **13** are very high leading and may not be accurate. These measurements have to be repeated. While the measurements for **11** needs to be further investigated, we observe that increasing polarity of the solvent leads to an increase of the fluorescence quantum yield. This could be due to better separation of the ionic liquid with increase of solvent polarity. However, we did not observe this trend with **10**.

CONCLUSION

A new ionic liquid based fluorescent PET sensor has been prepared during this study. This sensor has the advantage over other available sensors of its kind that its ionic liquid moiety makes it water soluble. The synthetic approach to the new sensor can be used to selectively functionalize 9 and 10 positions of an anthracene ring. Fluorescence studies of the new sensor indicate that the ionic liquid moiety does not interfere with the PET process of the sensor. Since the purification of the sensor after the final step is not satisfactory, future studies would involve developing a method to purify the final product and repeating the fluorescence experiments with the pure product.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 FT-NMR, All of the samples were obtained in $CDCl_3$ and the chemical shifts are reported in δ values (ppm) relative to TMS. Mass spectrometry was obtained from a Shimadzu LCMS-2020. The fluorescence spectra of the compounds were obtained using a Varian Cary Eclipse Fluorescence Spectrometer. The Cary 300 Bio UV-Vis Spectrophotometer was used to obtain absorption data.

Synthesis of 10-Methylanthracene-9-carboxaldehyde (**5**)

A mixture of 9-Anthracenecarboxaldehyde (**3**) (2.0g, 9.70 mmol), potassium hydroxide (3.0g, 53.47 mmol), hydrazine hydrate (5 mL), and ethylene glycol (50mL) was refluxed for one hour. After refluxing, the mixture was poured over ice and allow to cool overnight. Afterward, the yellow product **4** was vacuumed filtered and collected in 49% yield.

The Vilsmeier-Haack reaction was performed on **4**. 9-Methylanthracene (**4**) (0.40g, 2.08 mmol), dimethylformamide (0.41, 5.61 mmol), and phosphoryl chloride (0.86, 5.61 mmol), and dichloromethane (5mL) were stirred at room temperature overnight in a round bottom flask with a condenser attached. The reaction was quenched with sodium hydroxide (5 mL, 20%), extracted with dichloromethane, washed with water, and dried with magnesium sulfate. The dichloromethane was evaporated under vacuum to give **5** in 65% yield.

Synthesis of 1-methyl-3-((10-(morpholinomethyl)anthracen-9-yl)methyl)-1H-imidazol-3-ium chloride (**10**)

A mixture of 10-Methylanthracene-9-carboxaldehyde (**5**) (1.00, 4.54 mmol), N-bromosuccinimide(0.80g, 4.49 mmol), and benzoyl peroxide(0.057g, 0.24 mmol) in 20 mL dichloromethane was refluxed for two hours. After allowing the solution to cool to room temperature, 5 mL of chilled methanol was added. The mixture was stirred for an additional three minutes before being vacuumed filtered to give the yellow fluffy product **6** (1.23g, 90%).[1]H: δ 11.50 (s), 8.92-8.89 (m), 8.42-8.39 (m), 7.74-7.70 (m), 5.51 (s). [13]C: δ 193.40, 139.99, 131.59, 129.60, 128.41, 125.56, 125.41, 124.06, 123.79, 15.37.

Product **6** (0.60g, 2.00 mmol), triethylamine (0.20g, 2.00 mmol), and morpholine (0.17g, 2.00 mmol), were added to a round bottom flask with 10 mL of ethanol and refluxed overnight. The solution was allowed to cool to room temperature before dichloromethane (15 mL) was added. The mixture was then extracted with 3M HCl (2 x 10 mL). The aqueous layer was neutralized with potassium carbonate and a color change from orange to green was observed. The solid product **7** was obtained (0.51g, 83%) after vacuum filtration.[1]H: δ 11.52 (s), 8.93-8.90 (m), 8.64-8.61 (m), 7.71-7.59 (m).[13]C: δ 194.00, 134.14, 131.15, 130.95, 128.26, 127.24, 125.90, 125.77, 123.97. Calculated mass: 305.37 g/mol. Found m/z+1: 306.10 g/mol.

Product **7** (0.325g, 1.06 mmol) was reduced using sodium borohydride (0.081g, 1.06 mmol) in 50 mL of ethanol. After refluxing for one hour, the mixture was poured over ice to allow the product to crystallize. The solution was vacuumed filtered to give the pale yellow solid **13** (0.24g, 73%).[1]H: δ 8.58-8.55 (m), 8.49-8.45 (m) , 7.62-7.54 (m),

5.69 (s), 4.47 (s), 3.62 (s), 2.61 (s). ^{13}C: δ 131.65, 131.27, 130.82, 129.90, 125.97, 125.77, 125.36, 124.42, 67.11, 57.55, 54.61, 53.61. Calculated mass: 307.39 g/mol. Found m/z+1: 308.45 g/mol.

Compound **8** (0.15g, 0.49 mmol) was dissolved in 10 mL of dichloromethane before thionyl chloride (0.15g, 1.26 mmol) was added. The mixture was stirred at ambient temperature for 30 minutes. Excess thionyl chloride was evaporated under vacuum. Next, 50 mL of dichloromethane was added to the flask and the solution was transferred into a separatory funnel. Sodium bicarbonate (50 mL, 5%) was then added. The organic layer was dried over magnesium sulfate and the dichloromethane was evaporated under vacuum conditions to give product **9** (0.132, 85%). ^{1}H: δ 8.61-8.57 (m), 8.39-8.36 (m), 7.67-7.56 (m), 5.65 (s), 4.48 (s), 3.66 (s), 2.64 (s). ^{13}C: δ 131.89, 131.26, 129.62, 128.29, 126.44, 125.94, 125.49, 123.93, 67.13, 54.65, 53.65, 39.29.

Compound **10** was synthesized by dissolving **9** (0.20g, 0.61 mmol) in 7 mL of toluene before adding methyl imidazole (0.05g, 0.61 mmol) and refluxing for one hour. Afterward, the solvent was heated and evaporated under vacuum. Diethyl either (2 mL) was added to dissolve any excess methyl imidazole. The liquid was pipetted out and **10** was obtained (0.19g, 84%) after vacuum filtration. ^{1}H: δ 10.98 (s), 8.61-6.65 (m), 5.62 (s), 4.45 (s), 4.07 (s), 3.63 (s), 2.62 (s). ^{13}C: δ 131.79, 131.24, 130.61, 129.60, 128.31, 127.91, 126.45, 125.93, 125.51, 123.93, 123.34, 122.45, 121.10, 67.10, 54.61, 53.63, 39.30, 36.75. Calculated mass: 372.48 g/mol. Found (M-CH$_3$C$_3$H$_3$N$_2$): 290.3 g/mol.

Fluorescence studies of PET sensor **10**

A 10^{-5} M solution of compound **10** was prepared in water. About 20 mL of this solution was poured into a small beaker with a pH electrode and a small stir bar. Hydrochloric acid was added to bring the pH down to pH 2, where the fluorescent emission of the compound is maximized, and the fluorescent spectrum was recorded. Sodium hydroxide was then added to adjust the pH to regular intervals and the spectra were recorded up to pH 10.

Fluorescence Quantum Yields

Quantum yields of fluorescence were obtained using the equation:

$$\Phi_f = \frac{I_f(s)}{I_f(r)}$$

Where $I_f(s)$ and $I_f(r)$ are the integrated fluorescent intensities of the sensor and a reference, respectively. Solutions with concentrations of 10^{-5} M of the compounds **10-15** were used to record the UV spectrum at λ_{max} from 330-500 nm. A solution of 9,10-diphenylanthracene (reference) was prepared in 100% methanol by adding small amounts of the reference until the UV spectrum matchedclosely to that of the sensor. Then, the fluorescence spectra of each were recorded and integration was preformed. This was done at pH 2 and pH 10.
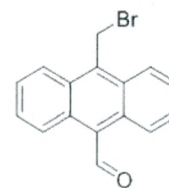
Figure 12: ^{1}H and ^{13}C spectra for compound **6**
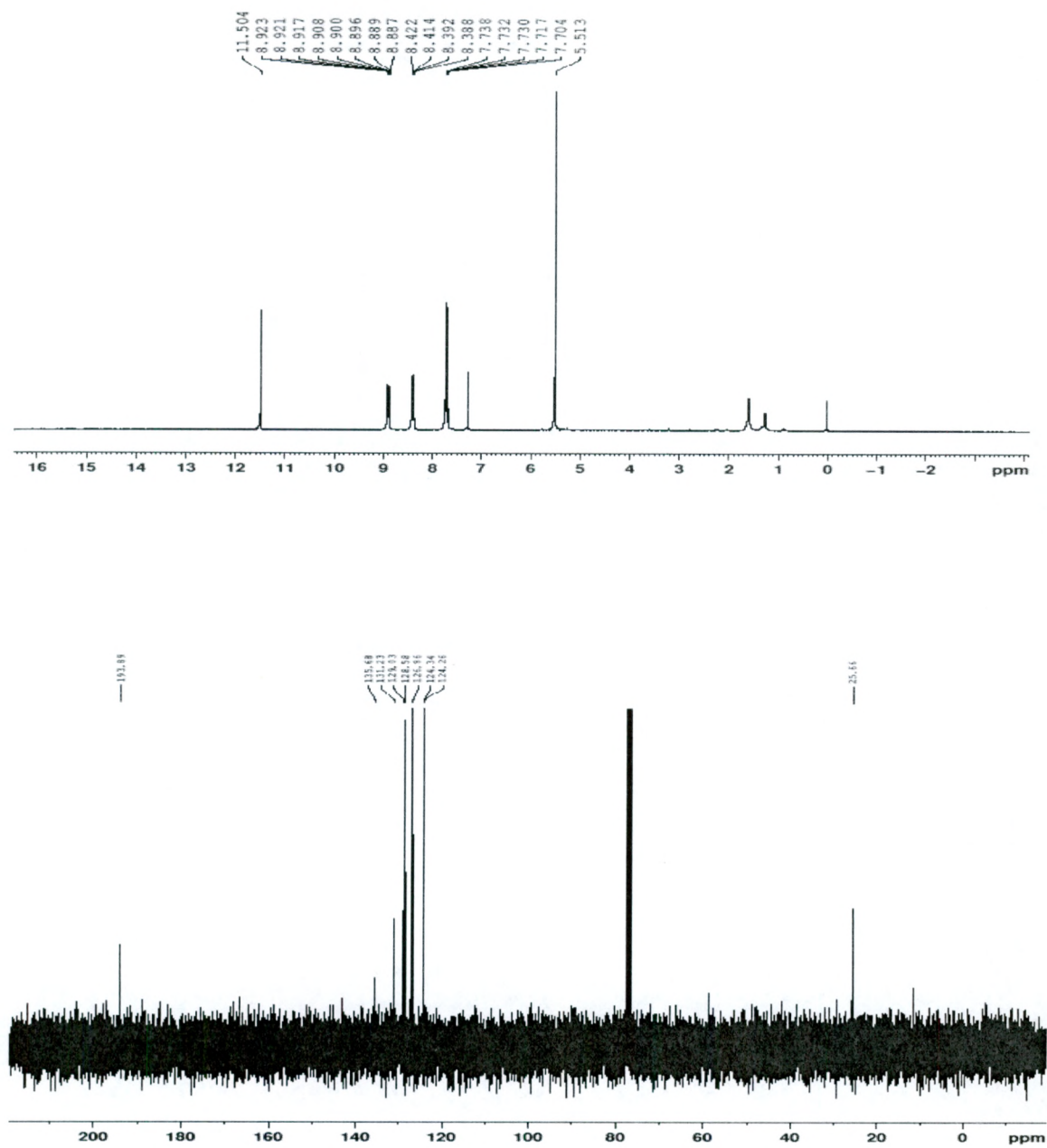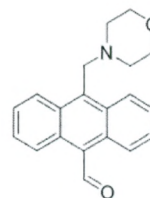
Figure 13: ^{1}H and ^{13}C spectra for compound **7**
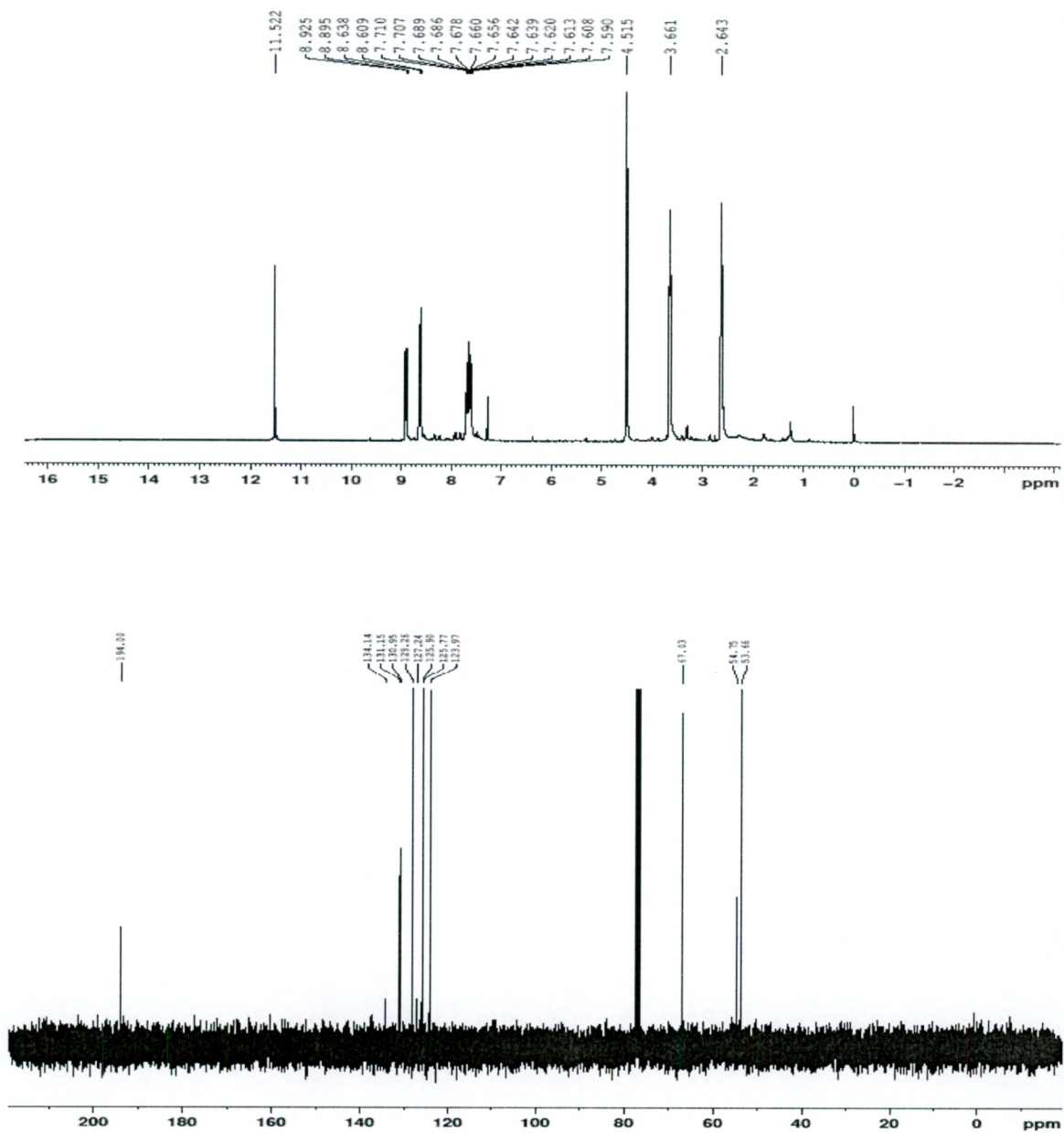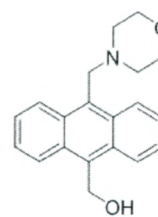
Figure 14: ^{1}H and ^{13}C NMR spectra of compound **8**
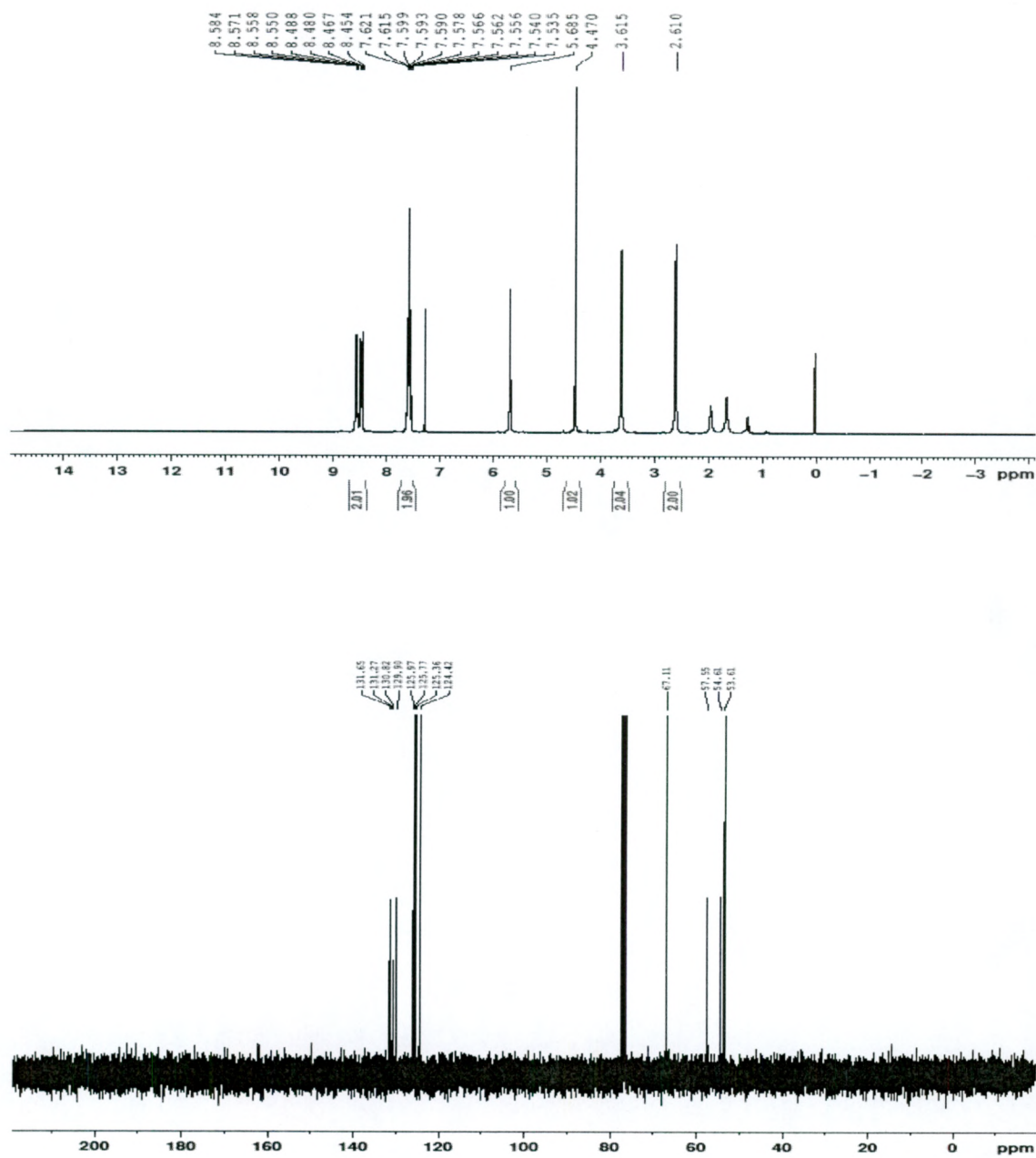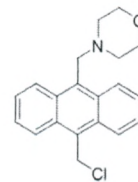
Figure 15: ¹H and ¹³C NMR spectra of compound **9**
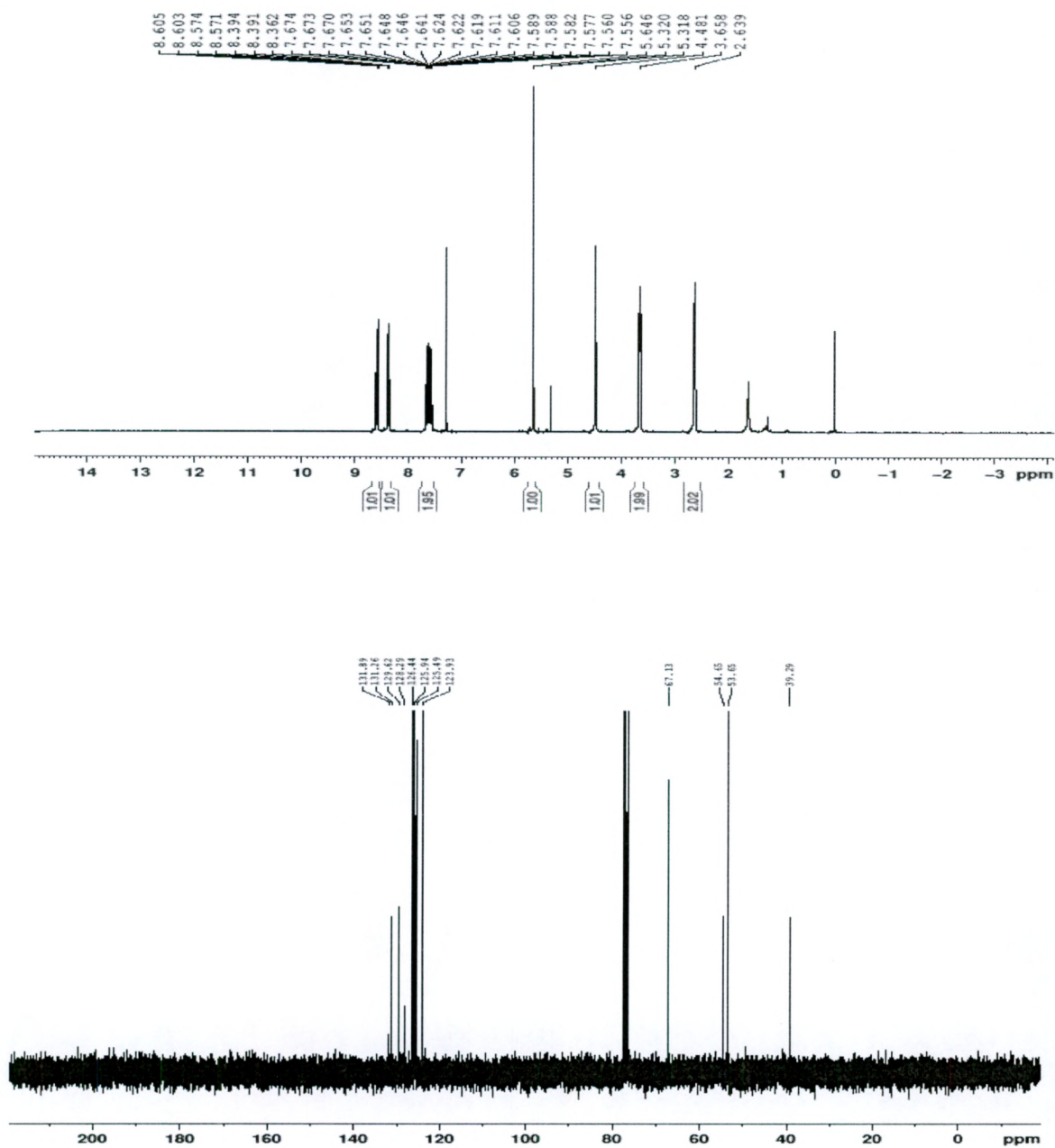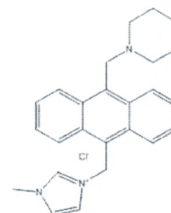
Figure 16: ^{1}H and ^{13}C NMR spectra of compound **10**
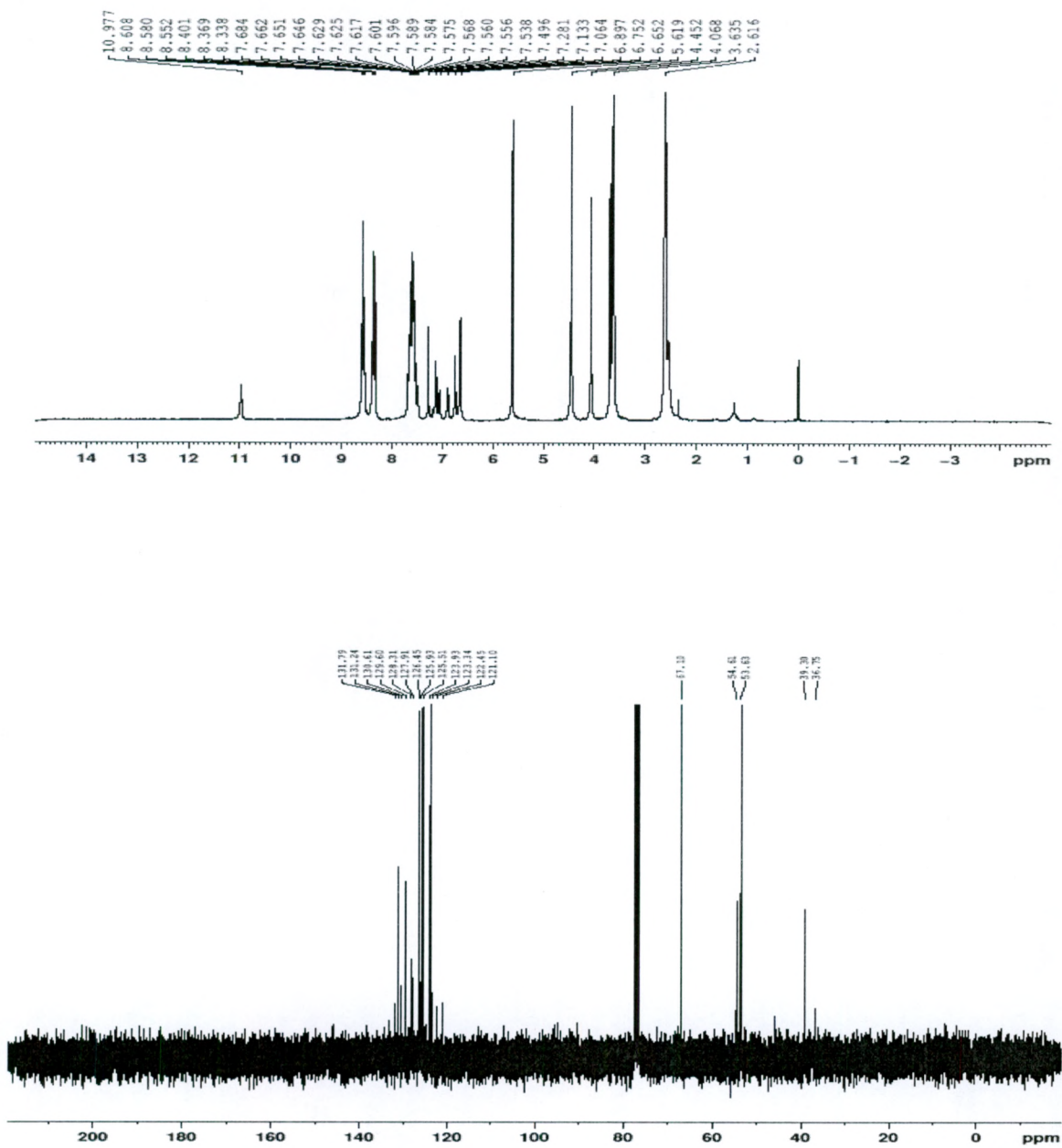
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