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Synthesis of a 4-(Trifluoromethyl)-2-Diazonium Perfluoroalkyl Benzenesuflonylimide (PFSI) Zwitterionic Monomer for Proton Exchange Membrane Fuel Cell

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Synthesis of a 4-(Trifluoromethyl)-2-Diazonium Perfluoroalkyl Benzenesuflonylimide (PFSI) Zwitterionic Monomer for Proton Exchange Membrane Fuel Cell

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Master of Science in Chemistry

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by

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ABSTRACT

Synthesis of a 4-(Trifluoromethyl)-2-Diazonium Perfluoroalkyl Benzenesuflonylimide (PFSI) Zwitterionic Monomer for Proton Exchange Membrane Fuel Cell

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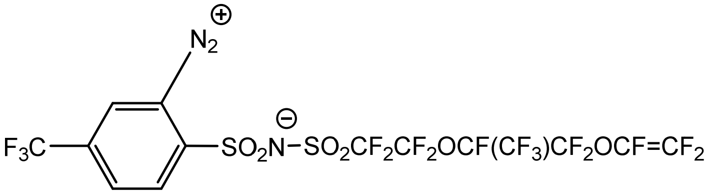
In order to achieve a more stable and highly proton conducting membrane that is also cost effective, the perfluoroalkyl benzenesulfonylimides (PFSI) polymers are proposed as electrolyte for Proton Exchange Membrane Fuel Cells. 4-(trifluoromethyl)-2-diazonium perfluoro-3, 6-dioxa-4-methyl-7-octene benzenesulfonyl imide (**I**) is synthesized from Nafion monomer via a 5-step schematic reaction at optimal reaction conditions. This diazonium PFSI zwitterionic monomer can be further subjected to polymerization. The loss of the diazonium N_2^+ functional group in the monomer is believed to form the covalent bond between the PFSI polymer electrolyte and carbon electrodes support. All the intermediates and final products were characterized using ^{1}H NMR, ^{19}F NMR and IR spectrometry.



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DEDICATION

This research work is dedicated to God Almighty, my mother, Mrs. Blessing Nworie, my siblings, and Antoine Barber.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Dr. Hua Mei for her patience, understanding, and motivation.

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LIST OF ABBREVATIONS

AFC	Alkaline Fuel Cell
DMF	Dimethylformamide
DMFC	Direct Methanol Fuel Cell
EW	Equivalent weight
FDZ	Functional Diazonium Zwitterion
FTIR	Fourier Transform Infra Red
GDL	Gas Diffusion Layer
Hz	Hertz
IEC	Ion Exchange Capacity
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
NMR	Nuclear Magnetic Resonance
PAFC	Phosphonic Acid Fuel Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFSA	Perflurosulfonic acid
PFSI	Perflurosulfonylimide
ppm	Parts per million
PTFE	Polytetrafluorethylene
SOFC	Solid Oxide Fuel Cell
TMS	Tetramethylsilane
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

The ability to convert chemical energy to electrical energy with reasonable efficiency is the main property associated with fuel cells. The advantages of these fuel cells show a decisive step towards replacement for the contemporary fossil fuel usage in the world [1]. Unlike the battery, the fuel cell does not need to be recharged as long as the right fuel is constantly supplied. It is fundamental to develop these fuel cells as they serve as an alternative source of power in stationary and portable devices. Generally, a fuel cell consists of an electrolyte that is squeezed between two electrodes (the anode and cathode), thus the generation of efficient electricity [2].

Table 1[3-5] compares the components and characteristics of different fuel cells. The electrolyte used is dependent on the type of electrochemical reactions involved, the operating temperatures, and also the application of the power produced.

Table 1: Types of Fuel Cells

Fuel Cells	Electrolytes	Fuel Used	Oxidant Used	Operating Temperatures
Polymer Electrolyte Membrane Fuel Cell (**PEMFC**)	H+ conducting membrane	H_2	Air, O_2	~80 °C
Alkaline Fuel Cell (**AFC**)	KOH	H_2	O_2	~100 °C
Phosphoric Acid Fuel Cells (**PAFC**)	Concentrated H_3PO_4	Natural gas, H_2	Air, O_2	~200 °C
Molten Carbonate Fuel Cells (**MCFC**)	Molten K_2CO_3	Natural gas, H_2	Air, O_2	~650 °C
Solid Oxide Fuel Cell (**SOFC**)	Z_2O_2	Natural gas, H_2	Air, O_2	800-1000 °C
Direct Methanol Fuel Cell (**DMFC)**	H+ conducting membrane	CH_3OH	Air, O_2	80-130 °C

Among these different fuel cells, polymer exchange membrane Fuel Cells (also called proton exchange membrane fuel cell, PEMFC) that employ a solid polymer electrolyte to separate the fuel from the oxidant have the potential to replace the internal combustion engine in vehicles and other power applications due to their energy-efficient, clean, and fuel flexibility characteristics [2]. The direct methanol fuel cell (DMFC) that has recently fast developed is basically similar to the PEMFC as it employs the polymer membrane as electrolyte. But as opposed to hydrogen gas fuel, pure liquid methanol is used with the formation of CO_2 as by product, and it greatly suffers from the very high rate of methanol crossover [6].

Due to good chemical and mechanical stability at lower temperature, Nafion, a perfluorosulfonic acid (PFSA) ionomer, is a known and widely used electrolyte membrane in the PEMFC [7]. The life span of this polymer will decrease over time because of the comparable weak physical integration between the fluoropolymer electrolyte and the carbon support.

This research targets synthesizing one analogue diazonium PFSI monomer (Figure 1) for PEMFC. Firstly, the diazonium PFSI monomer, which can attach the carbon electrode by covalent carbon-carbon bond, provides a promising approach to achieving a better intimate integration between the electrolyte and the electrodes for PEM fuel cells. Secondly, the PFSI polymers are proposed to replace Nafion for PEMFC. This is due to their greater thermal stability in the acid form, inertness to electrochemical conditions, and lower susceptibility to oxidative degradation and dehydration compared to other PFSA polymers [8].

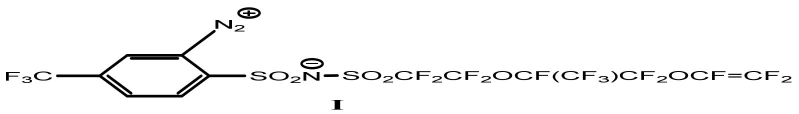

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Figure 1: Structure of Diazonium PFSI

PEM Fuel Cells (PEMFCs)

The reaction in PEM Fuel cells can be seen as a reversal of the electrolysis of H_2O to produce electricity when a catalyst is used. General electric's Thomas Grubb and Leonard Niedrach in the early 1950s invented the PEM technology, but its application as a power source was made evident in the U.S. space program in the 1960s [9]. Innovative processing schemes have improved the development of the PEM fuel cells over the years [10].

PEM fuel cells are regarded as promising sources of energy in their applications in mobile and stationary power usage due to their moderately low operation temperature with a great current density, tightly packed as a result of its small size, cost effectiveness, longer life span, and smooth start up [11].

In a reversible PEM Fuel Cell, the anode and cathode electrodes are been fed by hydrogen gas and oxygen gas respectively. The reaction products are formed at the cathode for PEMFC as shown in Figure 2 [12]. With a negligible production of CO_2 and almost no NO_x, HC and CO, PEMFC has proven to be a cleaner energy than the internal combustion engines. The PEMFC can be single, stacked, or designed as a system depending on the amount of voltage needed for its application [13].

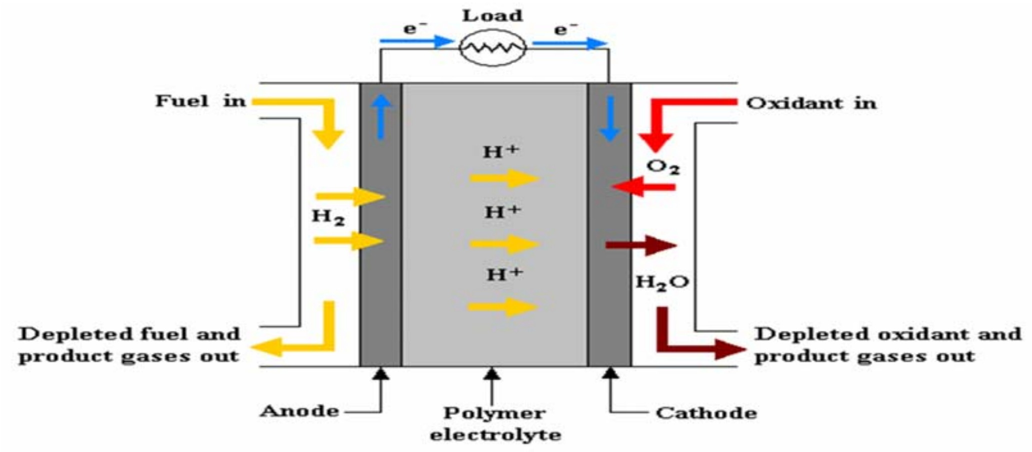


Figure 2: PEM Fuel cell. Used with permission [12].

The electrochemical reaction involves the oxidation of the hydrogen molecules at the anode in the catalyst layer (the catalyst's surface adsorbs hydrogen atoms from the hydrogen gas) to form protons and electrons. The electrons travel out of the cell to the outer circuit to produce electricity before re-entering the cathode. The protons are transferred to cathode through the proton conducting membrane to the catalyst layer (O_2 is adsorbed unto the catalyst's surface) where it combines with the reduced oxygen to produce water. The membrane is electrically nonconductive and thus does not allow the passage of electrons. The reaction occurring in the PEMFC is shown in scheme 1.

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$ … 1

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ … 2

Overall equation: $2H_2 + O_2 \rightarrow 2H_2O$ … 3

Scheme 1: The reaction occurring in a PEM Fuel Cell

The PEMFC operates at atmospheric pressure or even higher. Although higher temperatures have proven to increase the PEMFC performance, it does not specifically need high temperatures to be operational. This is because it undergoes an exothermic reaction whereby heat is generated as a by-product thus the excess heat needs to be removed by air or water cooling mechanism [8]. The PEMFC will be affected by contaminants in the fuel and in the air. Very tiny amounts of SO_2, NOx, H_2S at low temperature can be absorbed by the catalyst. Also, the performance of the cell can be reduced by poisoning the electrodes and membrane with contaminants like CO, CO_2 [14-15].

Components of PEM Fuel Cells

The PEMFC is made up of the bipolar plates and membrane electrode assembly (MEA) that comprise the Gas Diffusion Layer (GDL), catalyst layer, and proton exchange membrane. The electrochemical performance and efficiency of the electrodes is dependent on the modification of the MEA [16-18]. The transport system occurring in the cathode compartment of the MEA, as seen in Figure 3, includes; the movement of protons to the catalyst from the membrane, the passage of the electrons from the collector electrodes to the catalyst through the GDL, and the 'to and from' shuttle of the reactant and product gases in the catalyst layer and gas channels [19].

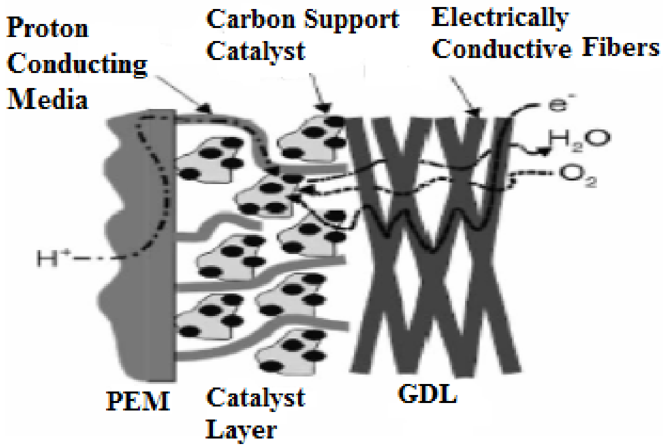


Figure 3: Expanded view of the Cathode part of the MEA Structure [19].

The gas diffusion layers allow the passage of the reactant gas from the bipolar plates to the catalyst layer with its porous layer characteristics. They also help to conduct electrons to the catalyst layer. Polytetrafluoroethylene (PTFE) is coated on electrode to prevent the accumulation of water in the GDL. It also controls the structure and porosity of the electrode. In the GDL, there is a diffusion of gases through the pores towards the electro-active layer.

The thin, porous catalyst layer plays an important role in the electrodes as it serves as the site for the half cell reaction occurring in PEMFC. The PTFE-based platinum in the catalyst layer increases the long-term performance of PEM FC [20]. The hydrophobic carbon powder and hydrophilic fluorinated polymer resin such as Nafion [21] present in the catalyst layer allowing the electrolyte to wet the carbon material permitting the diffusion of oxygen as air from the GDL to the electrolyte [22]. The performance of the catalyst will decrease when the catalyst layer is extremely hydrophobic and also when it contains too much of the electrolyte [23].

A diagram of a typical PEM fuel cell MEA comprising of the catalyst layers, proton exchange layers, and the gas diffusion layers is shown in Figure 4.

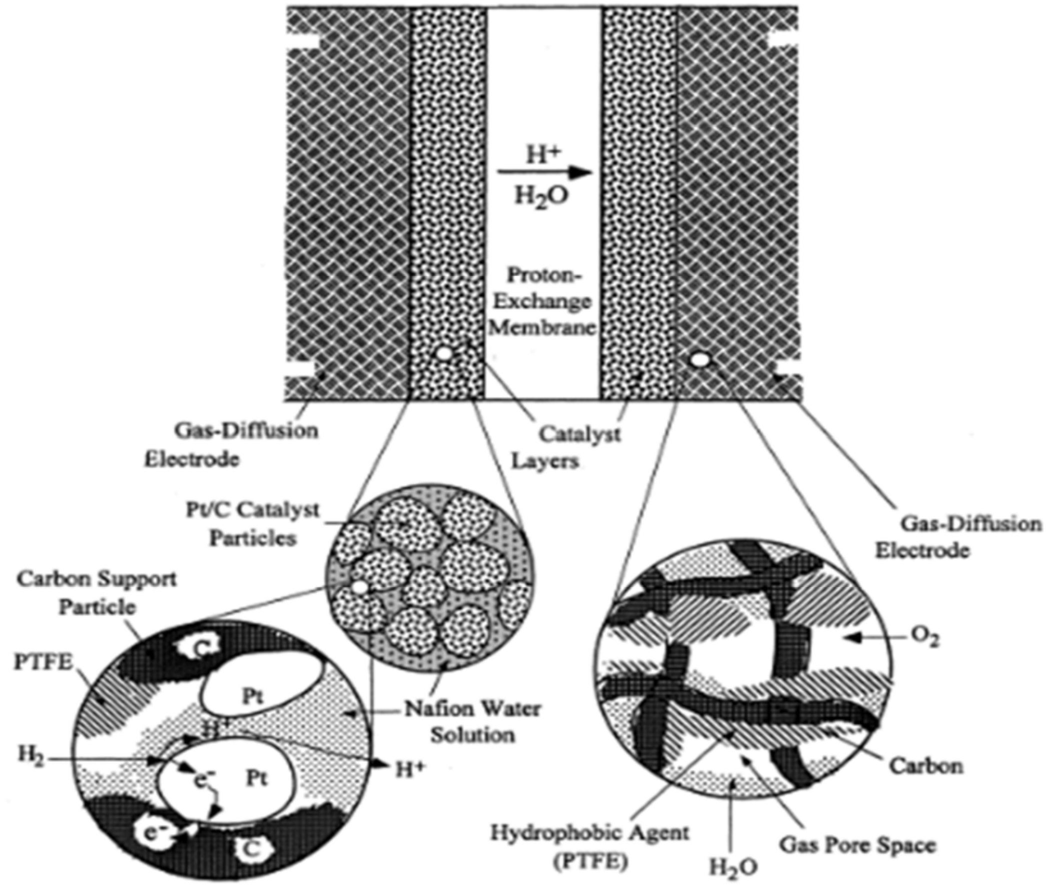


Figure 4: An overview diagram of the MEA structure (modified from Thampan) [12].

The basic requirements for PEMFC membrane include; good proton conductivity, excellent thermal, chemical and mechanical stability, low gas permeability, and cost effectiveness [24]. In addition to these characteristics, the membrane should be able to separate the fuel from the oxidant to avoid the mixing of the gases. Proton conductivities depends on the membrane’s morphology, water content, chemical structure, equivalent weight (EW=1000/IEC, IEC- ion exchange capacity), and the operating temperature. The durability of the PEMFC partly depends on the lifespan of the electrolyte membrane integration to the carbon electrodes [24].

Nafion Membranes

Most commercial electrolyte membranes of PEMFC such as Nafions are made up of the extrusive copolymerization of tetrafluoroethylene (TFE) with perfluorokyl (alkyl vinyl ether) based sulfonylic acid [25]. Other types of membranes also investigated by researches due to their special properties are the polyetherketones, polymides, and polyether sulfone [26, 27]. In the structure of Nafion, the perflurorinated alkyl backbones increase the chemical and thermal stability while the SO_3H pendant allows for better ionic conductivity (higher than 0.1Scm^{-}1 at 80 °C) [28]. Also, low dielectric constants, good better insulating ability in both oxidative and reductive conditions are added advantages of Nafions [28]. Nafions are commercially available in the sulfonic acid form ($-SO_3H$).

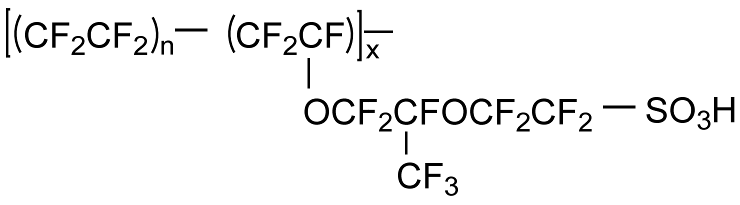


Figure 5: Chemical Structure of the Sulfonic form of Nafion

Limitations of Nafion as PEM Fuel Cell Membrane

Proton transfer in Nafion membrane depends on the dissociation of protons from the –SO_3H group in the presence of water [29]. Nafion membrane forms large rod-shaped micelles in water, and this disallows its passage into the micropores of the carbon's ionomer coatings in the MEA catalyst layer. Thus, they are 'washed out' overtime [11]. This leads to lower ion conductivity and reduced performance. Also, the sulfonic acid groups ($-SO_3H$) of the nafion decompose at higher temperatures by forming anhydrides ($-SO_2OSO_2-$). The electrolyte-to-carbon electrode integration (as there is no direct bonding of the electrolyte that is the solid nafion and the carbon support electrode at the catalyst layer) diminishes as a result of the oxidizing and highly acidic conditions that go on in the fuel cells' operations [30]. Due to its long process of casting and preparation, Nafion poses a high cost on PEMFC [31].

Platinum particles are the most commonly used catalyst in the PEMFCs. Traditionally, the catalyst efficiency usage is about 10-20% when Nafion is used as electrolyte for the PEMFCs [32]. The traditional dense electrode is as shown in Figure 6 [33].

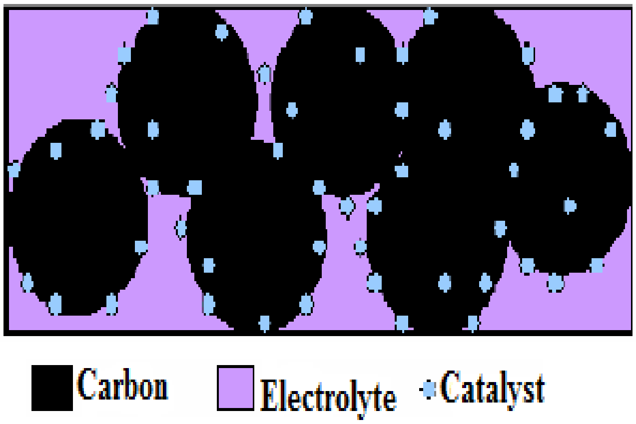


Figure 6: A Dense Carbon-Catalyst-Electrodes System in the PEMFCs. Used with permission [33].

Proposed PEM Fuel Cell Structure

Despite several efforts to improve the carbon electrode-electrolyte surface, such as applying the catalyst at close contacts with the membrane, using a thin film layer of the electrolyte on the electrodes surface, and increasing the active sites in the metal catalyst on the permeable electrode surfaces [34-36], the effective use of the expensive catalyst was not achieved.

A porous electrode, as seen in Figure 7, has been proposed recently to chemically graft the electrolyte onto the pores of the electrode [33]. This is believed to increase the use of the catalysts by allowing a better bonding.

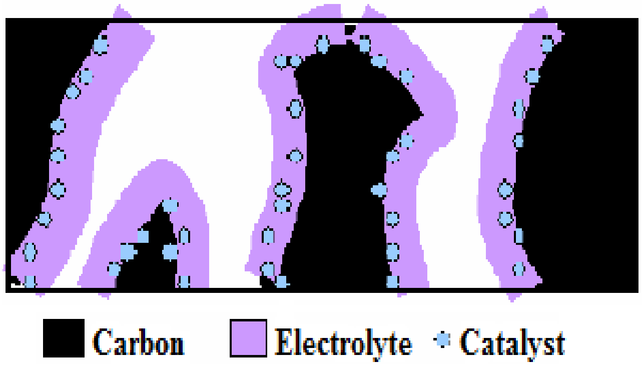


Figure 7: A Porous Carbon-Catalyst-Electrodes System in the PEMFCs. Used with permission [33].

Diazonium PFSI Zwitterions

Zwitterions are best described as molecules having substituent groups carrying ionic charges with the anion and cation contained in the same molecule. The zwitterionic amino acids posses both an amino and a carboxylic functional groups at the iso-electric point. Zwitterions posses an overall neutral charge [37].

$$\mathrm{RCH(NH_2)COOH} \longleftrightarrow \mathrm{RCH(NH_3^{+})COO^{-}}$$

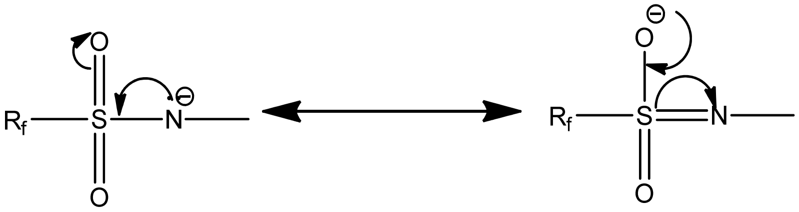
Scheme 2: Example of Amino Acid at the isoelectric point

Functional groups that contain significant charge being separated between directly bonded atoms are termed 'Semipolar'. Semipolar group are described as the possession of a filled orbital on one atom and an unfilled orbital on the other leading to them being distorted inductively by a charge separation that sometimes may be conjugated. These interactions decrease the polarity of semipolar groups below that of the pure dipolar form [38]. Hence, it is believed that Zwitterions increase the stability of large molecules.

PFSI Acidity Advantages

The Perfluoroalkyl sulfonic acids are commonly referred to as superacids as a result of the strong electron withdrawing perfluoroalkyl group [39]. These Perfluoroalkyl sulfonic acids have low pKa values. For example, the pka of Nafion 53 is close to -6 [40].

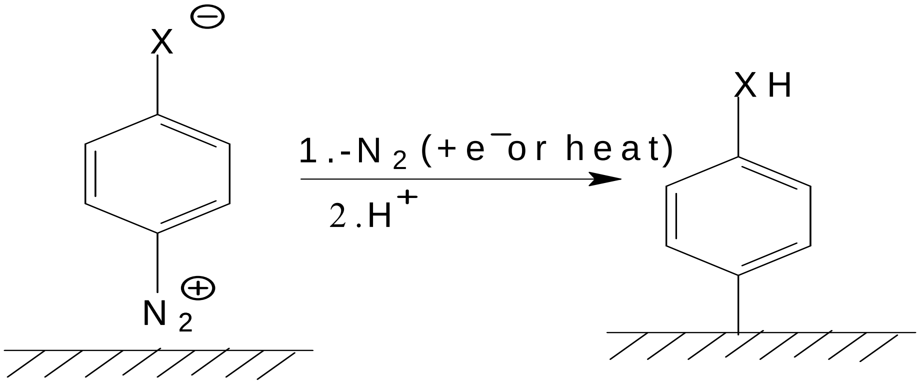
The trifluormethane sulfonyl group ($CF_3SO_2^-$) are believed to be strong neutral electron withdrawing group. One of the most acidic groups amongst other neutral acids in their gas phase are the $(C_4F_9SO)_2NH$ groups (pKa=19.8) [41]. The $(R_fSO_2)_2NH$ ($R_f \neq CF_3$) was earlier prepared by Meussdoerffer and Niederprum in the 1980s [42]. The polarisable substituent/anion interaction (P effect), correctly oriented dipolar substituent/anion interaction (F effect), and lastly, the substituent/ π-electron-acceptor interaction (R effect) that preferentially stabilizes the strong electron-pair donor anion forms compared to the corresponding weaker π-donor conjugate acid forms is believed to increase the gas phase acidity of the $(C_4F_9SO)_2NH$. The conjugate base of the PFSI $(Rf\text{-}SO_2)_2N^-$ is stabilized by the resonance effect. Hence, this accounts for the increase in acidity of the PFSI as seen in the scheme below.



Scheme 3: Charge delocalization in the conjugate base of PFSI

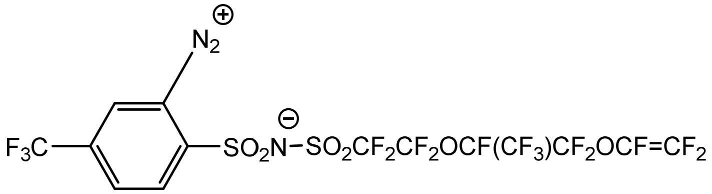
Diazonium PFSI Zwitterions Monomers

Diazonium PFSI zwitterionic monomers are proposed to improve the flexibility and ion exchange capacity necessary to attach the electrolyte to carbon as desired for PEM fuel cells. To replace the use of PFSA such as Nafion in PEMFCs, novel functional diazonium zwitterions containing the perfluoro sulfonimide groups were synthesized to chemically bond onto a modified carbon through grafting [11]. There is a covalent carbon-carbon bonding between the electrolyte and the carbon support by losing the diazonium group $-N_2^+$ via thermo or electro-chemcial reaction [43] as shown in scheme 3 where X is $SO_2N^-SO_2Rf$. An already synthesized $p-N_2^+PhSO2N^-SO_2CF_3$ monomer has been successfully grafted onto the carbon electrode [11].



Scheme 4: Grafting of the FDZ on carbon electrode

The PFSI monomers capable of undergoing further polymerization enhance the workability of the electrolyte. With an active diazonium group and a polymerizable functional group, there abound challenging but possible ways to design synthetic routes for the monomers than the small diazonium zwitterionic compounds. One analogue of diazonium perfluoroalkylsulfonimide (PFSI) monomer synthesized in this research is the 4-trifluoromethyl-3-diazonium perfluoro-3, 6-dioxa-4-methyl-7-octene benzenesulfonyl imide monomer (**I**) as shown in Figure 8. The synthesis method was used after various reaction conditions were tried in the lab.



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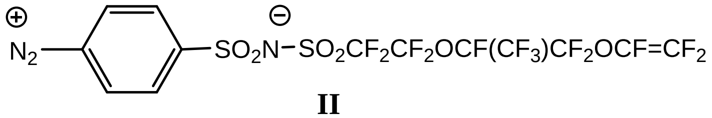

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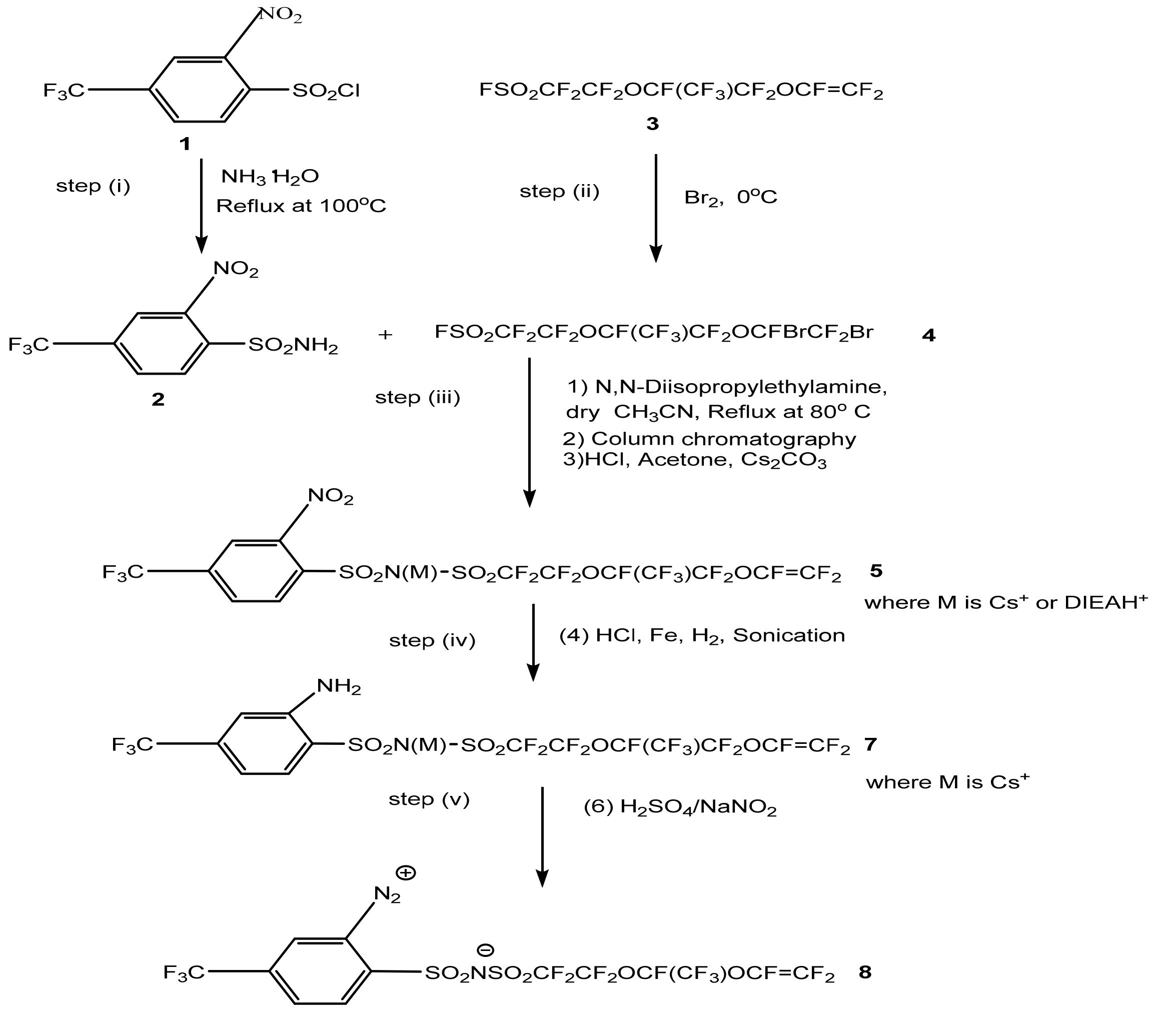
Figure 8: Structures of the two Diazonium Perfluorobenzene sulfonyl imide monomers

Bronsted-Lowry acidity is the capability of a compound to lose its proton [44]. It is believed that the acidity of the compound and the mobility of hydrogen increases with the presence of the electron withdrawing CF_3 substituent. Also, CF_3 group has a long-range acidifying factor because of its ability of producing a long-range electrostatic field that stabilizes the meta and para lone pairs in the conjugate base formed [45]. As earlier stated, the workable electrolyte membrane for PEMFC should have high proton conductivity so the presence of the substituted CF_3 group is proposed to increase the acidity of the modified functional diazonium zwitterions (FDZ). After further polymerization, this perfluoroalkylsufonimide (PFSI), **I**, can be compared with an already synthesized novel diazonium PFSI monomer, **II** [46] to compare their proton conductivity, reactivity and stability.

CHAPTER 2

RESEARCH AND DISCUSSION

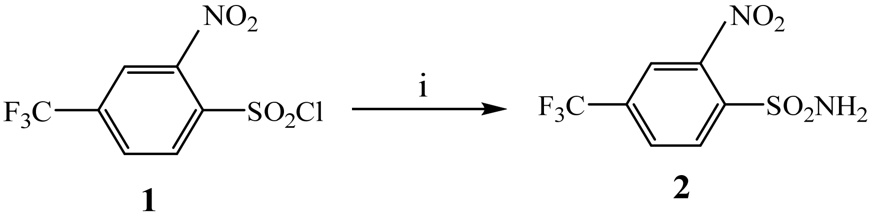
The synthesis of the diazonium PFSI monomer was prepared from two starting materials: 2-Nitro-4-(trifluromethane) benzenesulfonyl chloride and Nafion Monomer. This involves a five-step procedure: 1. an ammonolysis reaction, 2. a bromination reaction, 3. a coupling reaction followed by debromination , 4. a reduction reaction, and 5. a diazotization reaction. TLC was used to monitor the reaction progress of except the bromination and diazotization. The synthesized products were characterized by ^{1}H &^{19}F NMR and IR spectroscopy.



Scheme 5: Overall synthesis scheme

Ammonolysis Reaction

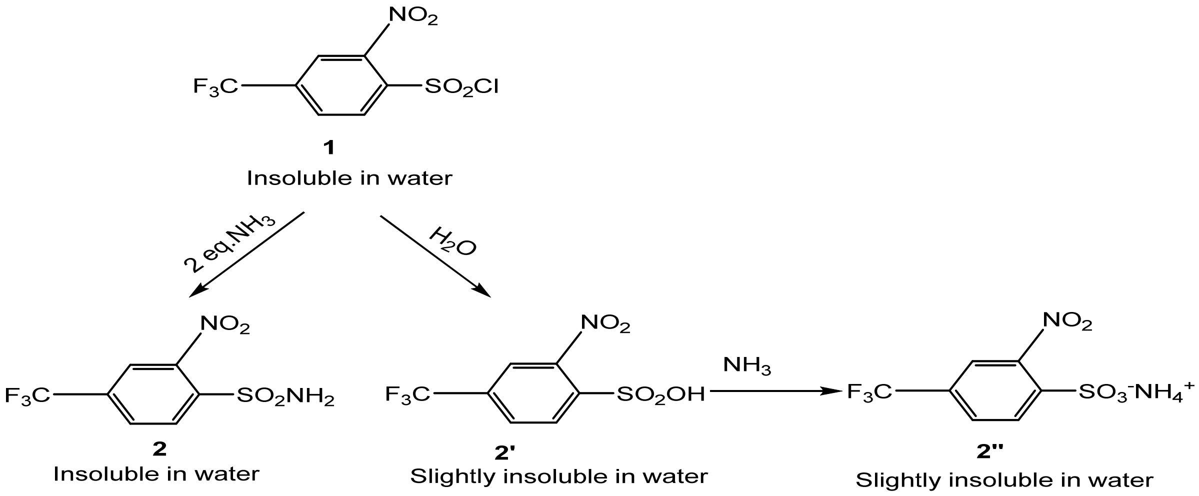
The conversion of 2-nitro-4-(trifluoromethyl)benzenesulfonyl chloride, **1** to 2-nitro-4-(trifluoromethyl)benzene sulfonyl amide **2** was carried out by refluxing it in the presence of excess ammonium hydroxide and acetonitrile at about 100 °C. The stoichiometric mole ratio of the aqueous ammonia to sulfonyl chloride is 2:1 respectively. This S_N2 reaction as seen in scheme 5 involves the replacement of the 'Cl$^-$'ions with the incoming –NH_2 group with the formation of HCl which is neutralized in the presence of the unreacted ammonia.



Scheme 6: Ammonolysis of 2-nitro-4-(trifluoromethyl) benzene sulfonyl chloride.

(i: Ammonia water, reflux at 100 °C overnight, 80%).

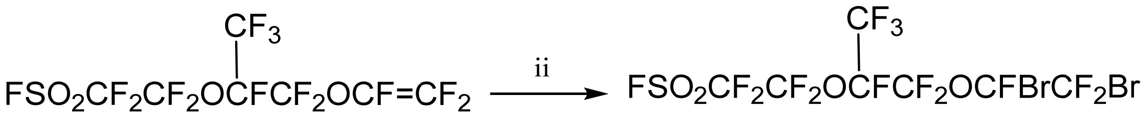
Ammonolysis reaction is more feasible than hydrolysis reaction because NH_3 is a better nucleophile than H_2O. Although the ammonolysis product was insoluble in water, the completion of this reaction was monitored. The impurity **2''**, as seen in scheme 7, comes from the hydrolysis of the 2-nitro-4-(trifluoromethyl)benzene sulfonyl chloride in aqueous solutions. Usually the hydrolysis impurities (the ammonium salt) can be removed easily through vacuum filtration. But because of the hydrophobic –CF_3 functional group on the benzene ring, the solubility of the hydrolysis product is decreased. Hence, the purification process is achieved through employing column chromatography or by recrystallization in water and acetonitrile.



Scheme 7: The hydrolysis reaction during Ammonolysis

Bromination of Nafion Monomer

The Nafion monomer **3**, that contains strong electron withdrawing perfluoroalkyl chain and perfluorovinyl ether group, is sensitive to bases at high temperature instead of acids like most alkenes. Protection of the double bond with bromine was achieved through a free radical reaction at a low temperature. Vacuum distillation was carried out to purify the brominated product **4**.

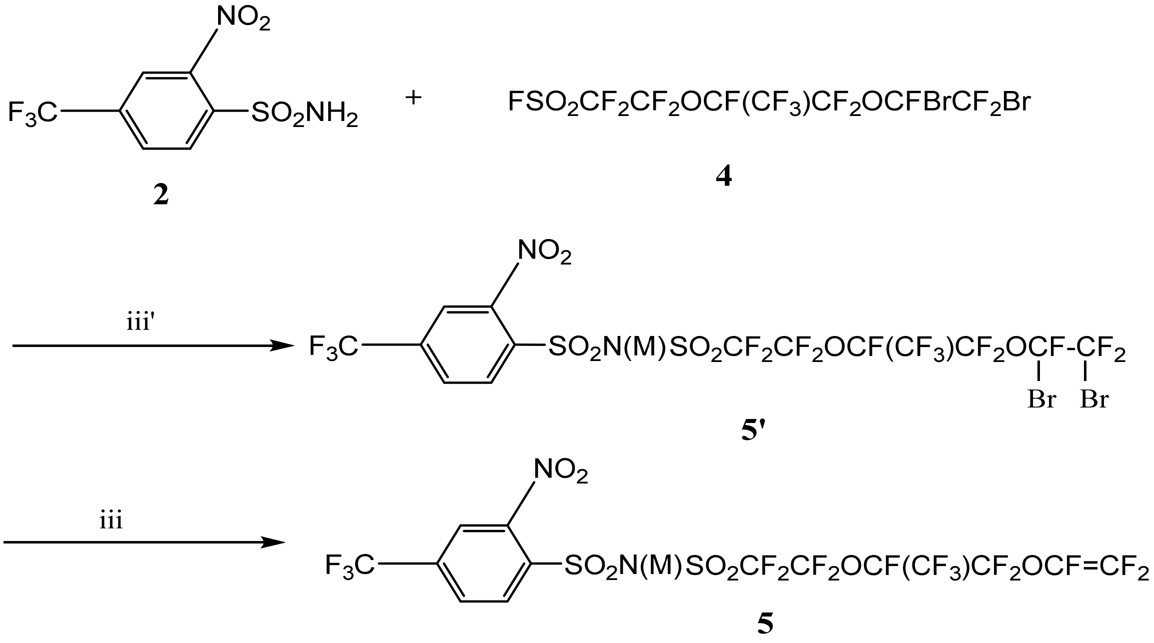


$$\underset{\mathbf{3}}{FSO_2CF_2CF_2O\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2} \xrightarrow{\text{ii}} \underset{\mathbf{4}}{FSO_2CF_2CF_2O\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2OCFBrCF_2Br}$$

Scheme 8: Bromination of Nafion monomer (ii: Br_2, 0 °C to r.t.)

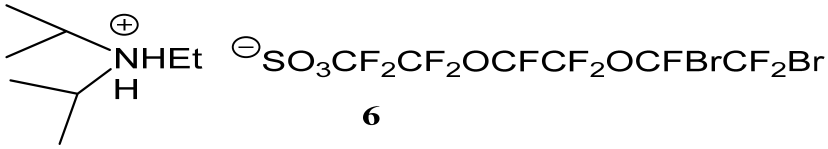
Coupling Reaction

In acidic medium, brominated nafion monomer **4** is comparably stable. At high temperature, the brominated nafion monomer does not only react with aryl sulfonyl amide but will be attacked by weak based catalysed water and form the hydrolysed product. The nucleophilicity of sulfonyl amide's $-SO_2NH_2$ is increased too when catalysed by an organic base, diisopropyl ethylene amine (DIEA).



Scheme 9: Coupling Reaction of 2-Nitro-4-(trifluoromethyl)benzene Sulfonylamide with Brominated Nafion Monomer [(iii': N, N-Diisopropylethylamine, dry CH_3CN, 80 °C for 3days; Column Chromatography), (iii: HCl, Acetone, Cs_2CO_3, at 70 °C for 30mins)]

In this S_N2 reaction, the hydrolysis product **6** as seen in Figure 9 can be greatly reduced by carrying out the reaction at extremely dry conditions with dry reagents and/or using extra amount of brominated nafion monomer **4**. Therefore, the stoichiometry requires 1 mole of sulfonyl amide to 1.02 mole of nafion monmer. It was to allow enough bromianted nafion monomer to react with the aryl sulfonyl amide.



6

Figure 9: Possible Hydrolysis By-product from Coupling Reaction.

The crude coupling product was sticky due to its DIEAH counterion. The purification process was carried out with column chromatography first to remove the excess starting material amide and then acidification and recrystallization with Cs_2CO_3 were used to remove the hydrolysis impurity.

In a previously synthesized diazonium PFSI zwitterionic monomer [46], the ^{19}F NMR spectrum showed two peaks for F**a** at δ -115 ppm, and δ -117ppm. The structure is shown in Figure 10. It was argued that the two peaks could be attributed to either the hydrolysis of the brominated nafion monomer or two diastereotropic fluorine atoms.

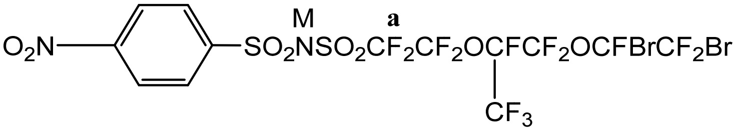
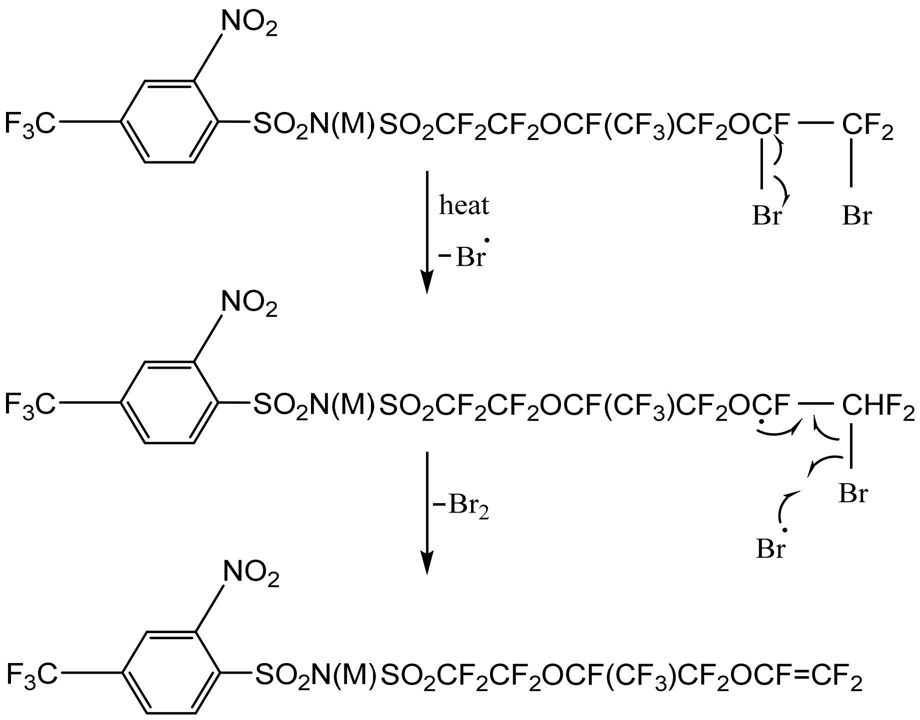


Figure 10: Structure of Coupling Product of the novel diazonium PFSI Zwitterionic monomer.

But according to the ^{19}F NMR spectrum of the coupling product **5**, there is only one peak for F**a**. It was suggested that either hydrolysis product **6** could be removed via column chromatography and recrystallization or there was no diasterotropic fluorine atom present in the compound's structure. Also, the debromination occurred with an appearance of the trifluorovinyl ether peaks at δ**f**-113ppm, δ**g**-121 ppm, and δ**g'** -135 ppm in the ^{19}F NMR spectrum.

The possible but inconclusive mechanism as seen in scheme 10 is through a free radical debromination that could have been facilitated by heating at about 70 °C employing the strong Cs_2CO_3 base to precipitate the coupling product **5**.

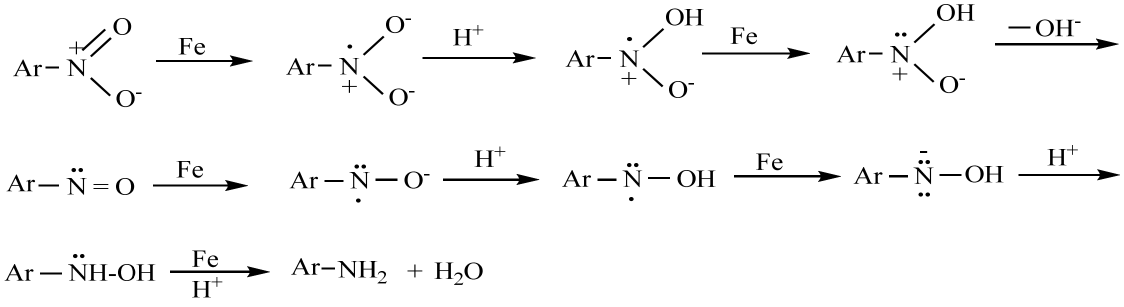


Scheme 10: Possible Debromination Mechanism

Reduction Reaction

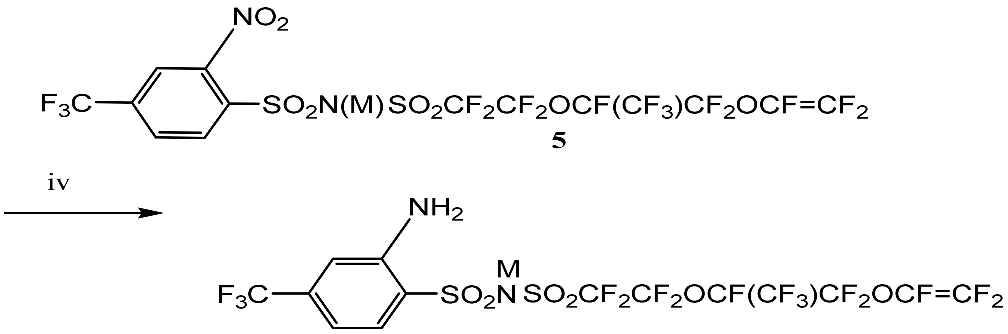
The reduction of the aromatic nitro compounds is one of the widely used methods for the preparation of the corresponding aromatic amines. Many reducing agents have been outlined in literatures [47]. The reduction of the nitro group can be achieved through various reagents such as: Fe/HCl or Fe/Acetic Acid, Zn/NaOH, Sn/HCl, Fe/ArOH, catalytic hydrogenation using Ni, Pd/C and PtO_2, sodium polysulfide, $NaBH_4$/Pt-Ni, and so on. Selecting which type of reagents to use is the contains limitation, ranging from harsh reaction condition, destruction of most sensitive functional groups, high cost and/or water-sensitivity, non-chemoselectivity in the reduction reactions [48].

Due to the perfluoro-vinyl ether group of the coupling product **5**, the use of Fe/HCl/H_2 gas in ultra-sound sonicator at room temperature was employed. Iron was chosen because it was fairly cheap and readily available. The reaction mechanism is shown in scheme 11 [63].



Scheme 11: Mechanism for reduction of Aromatic nitro-compounds

The reduction was carried out at room temperature because perfluorovinyl ether will react with acid at high temperature. Also the ultra-sound sonicator can help initiate the reduction reaction by removing the metal surface impurities [49].



7

Scheme 12: Reduction of the coupling product (iv: Hydrogen gas, Iron powder, Sonication, dry CH_3OH, r.t.)

The first trial of reduction using three equivalents of iron powder to the aromatic nitro compound yielded some impurities that were thought to be inter/intra molecular species of the reduced product as seen in Figure 11. And the protonated aryl –NH_3^+ would be converted back to –NH_2 after basifying with 10% NaOH. But the impurities persisted according to the ^1H NMR spectrum.

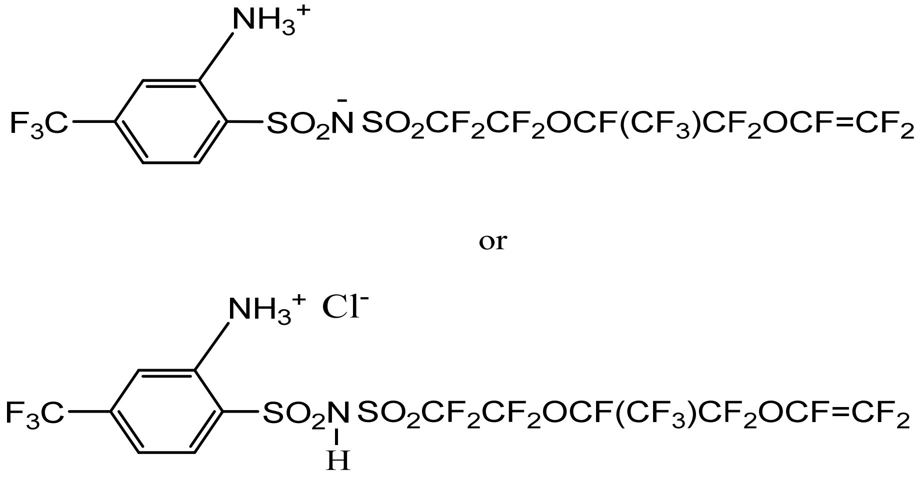
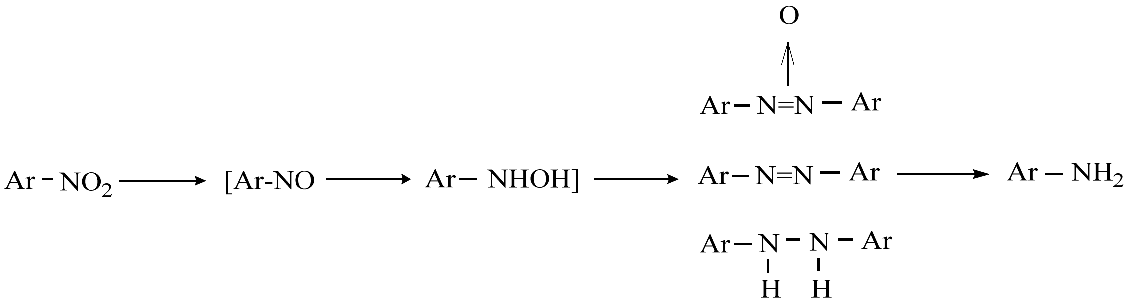


Figure 11: Possible inter/intra molecular interactions occurring with the reduced product **7**

Another hypothesis is the presence of the intermediates as see in scheme 13 [50]. Due to the similar polarity of the impurities and the product, purification via column chromatography failed.

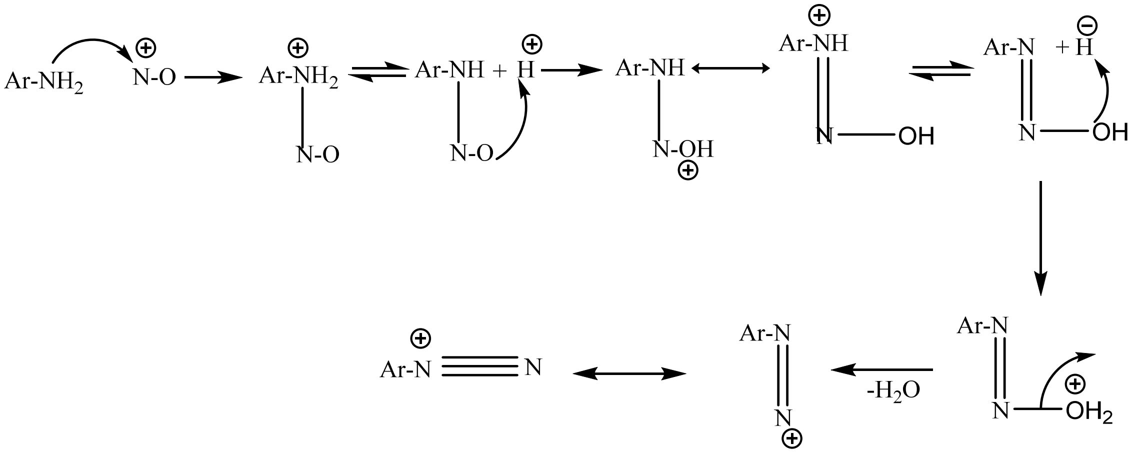


Scheme 13: The Hydroxylamine, azoxy and azo compounds intermediates.

The second trial was conducted with excess iron powder (7:1 of the Fe powder to coupling product) at the same reaction conditions as the first trial. Although the reaction was completed according to ^1H and ^{19}F NMR spectra, the purification of the product by vacuum filtration failed. The possible reason is that the brown jelly like product formed with the excess iron. The optimal reaction condition was finally established with the ratio 5:1 of iron powder and the coupling product **5** in the presence of HCl and methanol mixture for about 2 days promoted by sonication as in scheme 12.

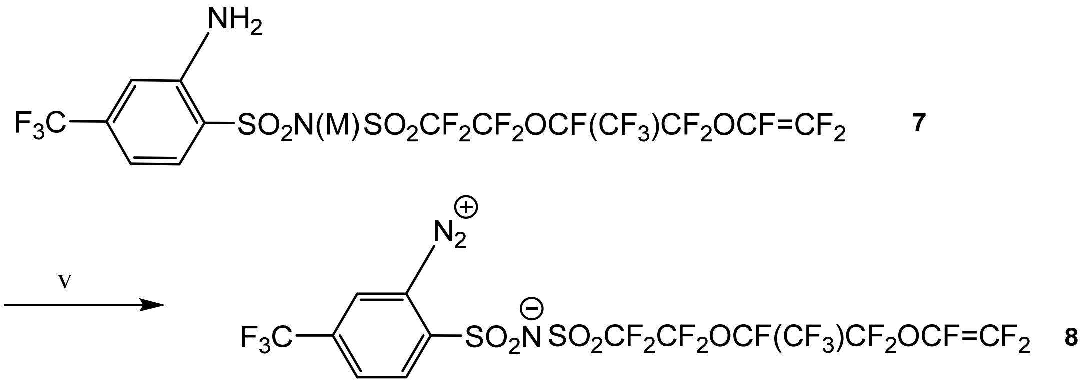
Diazotization

Diazonium reactions are usually performed by converting primary amine using nitrous acid HNO_2 (HONO) to form the diazonium salts [51]. Although small diazonium compounds are susceptible to explosion, the big diazonium compounds are comparably stable [51]. The HNO_2 can be produced by reacting sodium nitrite with aqueous mineral acid. The actual diazotization reagent is the nitosonium ion, NO^+ and this is formed in situ. The reaction mechanism is shown in scheme 14 [52].



Scheme 14: Diazotization of 1° Aromatic Amines mechanism.

For this reaction, conc. HCl was first tried but failed because of the poor solubility of the reduced product **7**. Therefore, conc. H_2SO_4 was used to carry out the reaction. The reason is that H_2SO_4 is a very polar liquid with dielectric constant 100 [52]. And thus, it is a better solvent to dissolve the polar reduced product **7** for this reaction. This reaction requires low activation energy, so it was carried out at low temperature of about 0-5 °C. Although the reaction can be quite slow at low temperature, if it is done at higher temperatures, it will lead to the decomposition of the nitrous acid (HONO) because HONO is not stable at room temperature [53].



Scheme 15: Synthesis of the diazonium compound (v: HCl, $NaNO_2$, 0 °C).

CHAPTER 3

EXPERIMENTAL

General Considerations

NMR Spectroscopy

^{1}H and ^{19}F NMR spectra were measured on a Joel JNM-ECP 400 MHz FT NMR spectrometer using CD_3CN as solvent. Chemical shifts are reported in parts per million (ppm), and the coupling constants are reported as a 'J' value in Hz. ^{1}H NMR chemical shifts were referenced against TMS. ^{19}F NMR chemical shifts were referenced against a $CFCl_3$ external standard. The splitting patterns of resonance were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m).

The NMR spectra were measured using 1-2 mmol/L concentrations of the solutions (unless indicated otherwise) and small amounts of $CFCl_3$ gas in an appropriate deuterated solvent for ^{19}F NMR only.

Infra-red Spectroscopy

The infrared spectra were recorded on the Shimadzu 1R Prestige-21 FTIR spectrometers. Solid samples were prepared as fine powder. Unless indicated otherwise, samples were a minimum of 99.5% pure by ^{1}H and ^{19}F NMR. IR spectra were scanned from 4000 cm-1 to 450 cm-1 and reported in wavenumbers (cm-1) with intensity abbreviations: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

Gas Chromatography-Mass Spectrometer

GC-MS were recorded on Shimadzu GCMS-QP2010 Plus GC system spectrometer. The samples were prepared by dissolving 1 mg of the solid samples in 1 mL of acetone.

Thin Layer Chromatography

Thin Layer Chromatography (TLC) was conducted using UV active silica gel plates in suitable solvents. The readout was carried out under UV lamp.

Glass Vacuum System

The distillation, drying, sublimation, purge, and trap procedures for volatile compounds were carried out on a glass vacuum line. This high vacuum line system as seen in Figure 12 having several stop cocks alongside connected to a diffusion pump is equipped with Teflon. It consists of two manifolds where one manifold is for the vacuum and the other is for the nitrogen gas. A good vacuum of about 10^{-4}-10^{-7} torr can be achieved.

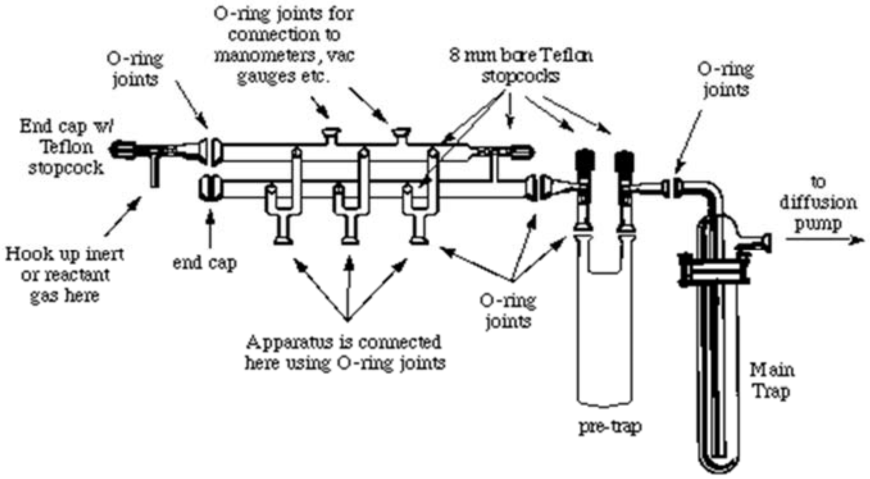


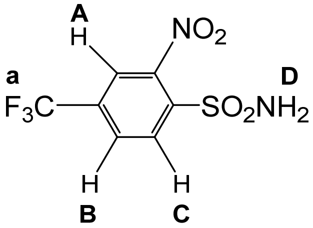
Fig. 12: Line Diagram of 2- manifolds glass vacuum line. Used with permission [54].

Purification of Solvent and Experimental Practice

The starting materials: p-nitro benzene sulfonyl chloride Nafion Monomer ($FSO_2CF_2CF_2OCF_2CF(CF_3)OCF=CF_2$) were commercially bought from sources and used as received unless indicated otherwise. All the reactions were performed in glassware unless indicated otherwise. Air or moisture sensitive compounds were used in a dry box under nitrogen. Solvents were dried by heating at elevated temperatures under vacuum.

Synthesis of 2-Nitro-4-trifluoro benzene sulfonyl amide

In a typical procedure, (2.0 grams, 6.9 mmoles) of 2-nitro-4-benzene sulfonyl chloride was added to a 100 mL round bottom flask equipped with a stir bar. Then 30 mL of Ammonia hydroxide (28-30%) and 22.65 mL of acetonitrile were added to the round bottom flask. The solution was refluxed at about 100 °C overnight. The acetonitrile was removed by rotary evaporator. The crude product was vacuum filtered with 3 X 15 mL of water. The product was then vacuum dried overnight. TLC using the 1:1 hexane to acetone revealed two spots with Rf values of 0.38 and 0.67 (product). The final product (1.47 g, 79.1%) was obtained as a yellow solid after it was recrystallized with acetonitrile and water as solvents.



^{19}F NMR (400 MHz; CD_3CN; ppm): δ_a -62.42 (3F,s).

^{1}H NMR (400 MHz; CD_3CN; ppm): δ_A 8.21 (1H, s), δ_B 8.27 (1H, d), δ_C 8.10 (2H, d), J_{BC} = 6 Hz, δ_D 6.24 (2H, s).

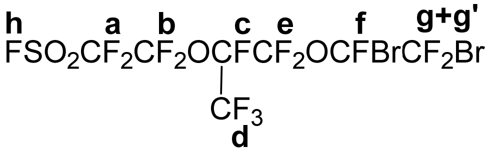
IR (ν_{max}/cm^{-1}): 3363.86m (NH), 1537s and 1329s (NO), 1161.15s and 1138s (S=O).

m/z: 254(M^{+}, 100%), 206, 75, 64, 50.

Synthesis of $FSO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$

In a typical procedure, the Nafion monomer $FSO_2CF_2CF_2OCF_2CF(CF_3)OCF=CF_2$ (5.0 grams, 11.14 mmloes) was added into a 50 ml round bottom flask equipped with a stir bar and placed in an ice bath at 0°C. Then bromine (1 mL, 19.49 mmoles) was added slowly using a pressure-equalizing funnel over the course of 2 hours. Excess Bromine was determined as a reddish colour stayed for 30 minutes. The excess bromine remained in the funnel and as the reaction was allowed to continue overnight in the presence of light, some bromine vaporized and was made available as Br_2 encouraging some free radical reaction.

The excess bromine was reduced by slowly adding 5% $NaHSO_3$ solution until the reddish color disappeared. A separatory funnel was used to obtain the organic layer that remained at the bottom by washing three times with 5 mL DI water. Na_2SO_4 was added to dry the product that was later distilled at 100 °C under dynamic high vacuum. A percent yield of 70.9% (4.89 grams) was obtained.

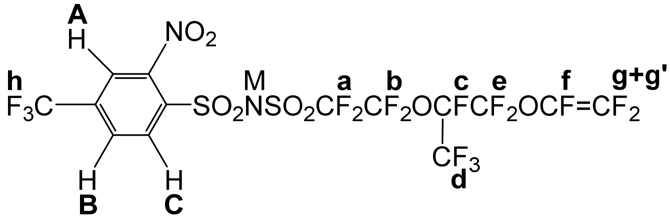


$$\mathrm{FSO_2CF_2CF_2O\underset{\underset{CF_3}{|}}{C}FCF_2OCFBrCF_2Br}$$

^{19}F NMR (400 MHz; CD_3CN; ppm): δ_a-110.76 (2F, m), δ_b -72.35 (2F, m), δ_c -143.4 (1F, m), δ_d -77.87 (3F, qm), δ_e -79.05 (2F, AB pattern multiplet), δ_f -72.61 (1F, m), δ_g-64.18 (2F, d), δ_h 45.88 (1F, s).

Synthesis of 4-CF_3-2-$NO_2PhSO_2N(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$

In a typical procedure, 1.025 grams (1.64 mmoles) of the brominated nafion monomer, 0.43 grams (1.61mmoles) of the 2-nitro-4-trifluorobenzenesulfnoyl amide were added into a three-necked round bottom flask equipped with a stir bar and two rubber septa in a dry box. Then 10 mL of acetonitrile and 15 mL of diisopropyl ethylamine (DIEA) were injected into the closed flask. The solution was refluxed for 3 days at 100° C in a closed system. The reaction was monitored with TLC in 1.5:1 acetone to hexane, which revealed three spots with an Rf values of 0.70, 0.64 and 0.29. The solvent was removed by rotate evaporator. The crude coupling product was then recrystallized with 1 gram of Cs (6.50 mmoles) in 3 mL of water and 20 mL of acetone at 70 °C for 20 minutes. The 1.5:1 ratio of acetone to hexane was used to run through the column to remove the hydrolysis by-product. The amber solid product (1.66 grams, 74 %) was obtained after removing the solvent and drying under dynamic high vacuum for overnight. M represents such as Cs^+, $DIEAH^+$.



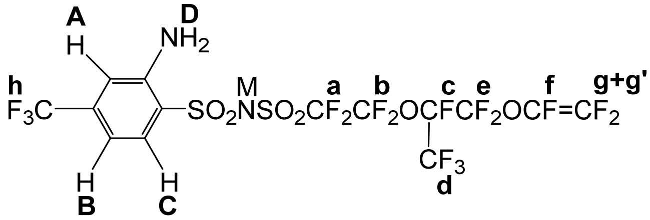
^{19}F NMR (400 MHz; CD_3CN; ppm): δ_a -115.43 (2F, m), δ_b -77.53.0 (2F, m), δ_c -144.58 (1F, m), δ_d -79.21 (3F, qm), δ_e -83.96 (2F, AB pattern multiplet), δ_f -113.05 (1F, d), δ_g -121.17 (1F, q). $\delta_{g'}$-135.79(1F, q) δ_h-62.43 (3F, qm)

^{1}H NMR (400 MHz; CD_3CN; ppm): δ_A 8.00 (1H, s), δ_B 8.28 (2H, d), δ_C 7.98 (2H, d) J_{BC} = 6 Hz.

IR (ν_{max}/cm^{-1}): 1541.12s and 1323.17m (NO), 1138vs (CF_2), 1064vs, 1122.57vs and 1288.45w (S=O).

Synthesis of 4-CF_3-2-NH_2-$PhSO_2N(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$

In a typical procedure, 0.25 grams (.217 mmoles) of the coupled product and 0.07 grams (1.37 mmoles) of iron powder were added to a 50 ml one-necked round bottom flask equipped with a stir bar. And then, 20 mL of methanol and 1 mL of HCL were added to the round bottom flask subsequently. The flask was equipped with a septum, a needle, and a H_2 gas filled balloon. The reaction was run at room temperature in ultrasound sonicator for 2 days. TLC was used to monitor the reaction in 1.5:1 acetone to hexane, which revealed one spot with an Rf value of 0.09. The excess iron powder was filtered out by vacuum filtration. The organic portion was extracted out with 3x 10 mL of ethyl acetate from water. Finally, the brown purified product (0.36 grams, 73%) was obtained after removing solvent again by rotate evaporator and drying with dynamic high vacuum for 4 hours. M represents Cs^+ and other cations, such as $DIEAH^+$. The product is very sticky. It also contains impurity $CH_3COOCH_2CH_3$.



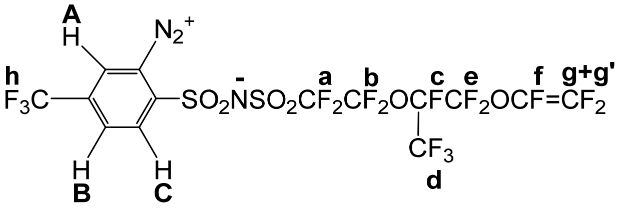
^{19}F NMR (400 MHz; CD_3CN; ppm) δ_a -116.85 (2F, m), δ_b -78.88 (2F, m), δ_c -145.73 (1F, m), δ_d -80.20 (3F, qm), δ_e -85.14 (2F, AB pattern multiplet), δ_f -113.79 (1F, d), δ_g -122.50 (1F, q). $\delta_{g'}$-136.90(1F, q) δ_h-63.41 (3F, qm)

^1H NMR (400 MHz; CD_3CN; ppm): δ_A 7.05 (1H, s), δ_B 7.79 (2H, d), δ_C 6.89 (2H, d) J_{BC} = 6 Hz, δ_D 5.5 (2H, s)

IR (ν_{max}/cm^{-1}):3431.36m and 1635.64s (NH), 1325.17m and 1076.28vw (S=O), 1232.51s and 1132.21vs (CF_2).

Synthesis of 4-CF_3-2-N_2^+ $PhSO_2N^-SO_2CF_2CF_2OCF$ (CF_3)$CF_2OCF=CF_2$)

In a typical procedure, 0.15 grams (0.237 mmoles) of debromination product**,** 0.173 grams (2.275 mmoles) of $NaNO_2$, and 3 ml of H_2SO_4 were added in a 50 ml round bottom flask equipped with a stir bar. The solution was stirred for 2 hours in the ice bath and then poured into ice before vacuum filtration. The final purified product (0.044g, 56%) was obtained after drying under dynamic vacuum line for 8 hours.



^{19}F NMR (400 MHz; CD_3CN; ppm): δ_a -115.32 (2F, m), δ_b -77.89 (2F, m), δ_c -144.23 (1F, m), δ_d -78.50 (3F, qm), δ_e -83.73 (2F, AB pattern multiplet), δ_f -112.44 (1F, d), δ_g -120.80 (1F, q). $\delta_{g'}$-135.52 (1F, q) δ_h -62.75 (3F, qm)

^{1}H NMR (400 MHz; CD_3CN; ppm): δ_A 8.94 (1H, s), δ_B 8.64 (1H, d), δ_C 8.54(1H, d) J_{BC} = 6 Hz.

IR (ν_{max}/cm^{-1}): 2301.08w ($N\equiv N$), 1337s, 1283w and 1076vs (S=O), 1147vs (CF_2)

CHAPTER 4

CONCLUSION

One new perfluoro alkyl sulfonyl (PFSI) diazonium zwitterions monomer was synthesized and characterized. This can permit a new path to designing synthetic schemes for other diazonium zwitterions or providing opportunities to graft this monomer (which could be further subjected to polymerization) to the nanoporous carbon/Pt catalyst via the diazonium salt either by electrochemical reduction or thermal decomposition. This will afford the formation of a covalent carbon-carbon bond proposed for the PEM Fuel Cell. This is believed to increase the commercialization of the PEM fuel cells.

The extra peak found at -117ppm in the synthesis of the novel diazonium PFSI zwitterionic monomer as stated earlier is the hydrolysis product and can be eliminated during the recrystallization step. The debromination of the protected per fluoro vinyl ether was perceived to have occurred via heating during the recrystallization of the crude coupling product that shortened the overall reaction scheme. Additional recrystallization experiments will be performed on different synthesized coupling products to support this hypothesis.

REFERENCES

[1] Crabtree G W.; and Daresselhaus, M. S. The Hydrogen Fuel Alternative. MRS Bull. **2008**, 33, 421-428

[2] Hickner, M.; Ghassemi, H.; Kim, Y.S.; Einsla, B.; McGrath, J.E. Alternative Polymer Systems for Proton Exchange Membranes (PEMs). Chem. Rev. **2004**, 104, 4587-4612.

[3] National Energy Technology Laboratory, Science Applications International Coporation-US Department of Energy, Parson, Fuel cells hand book, EG&G Services, Office of Fossil Energy, 5th ed,; 2000.

[4] Acres, G. J. K.; Frost, J. C.; Hards, G. A.; Potter, R. J.; Ralph, T. R.; Thompsett, D.; Burstein, G. T.; Hutchings, G. J. Electrocatalysts for Fuel Cells. Catal. Today, **1997**, 38.

[5] Ralph, T. R.; Hards, G. A. Fuel cells: Clean Energy Production for the New Millennium. Chem Ind, Lond, **1998**, 8, 334.

[6] Kim, J.; Kim, B.; Jung, B. Proton Conductivities and Methanol Permeabilities of Membranes Made from Partially Sulfonated Polystyrene-block-Poly(ethylene-ran-butylene)-block-Polystyrene Copolymers. J. Membr. Sci. **2002**, 207, 129-137.

[7] Moilanen, D. E., Spry, D. B., Fayer, M. D.Water Dyanmics and Proton Transfer In Nafion Fuel Cell Membranes. Langmuir **2008**, 24 [8], 3690-3698.

[8] Ryan Baker and Jiujun Zhang Institute for fuel cell innovation. National Research of Canada, 4250 Wesbrook Mall, Vancouver, British Columbia V6T 1W5, Canada, 2011.

[9] Hyder, A. K.; Sabripour, S.; Flood, D. J., Halpert, G., Wiley, R. L., Spacecraft Power Technologies, Imperial College Press, World Scientific Publishing Co, Pte, Ltd.; 2003, 224.

[10] Barbir, F. PEM Fuel Cells: Theory and Practice,1st ed.; Elsevier Academic Press: New York, 2005.

[11] Hua, Mei, Perfluoroalkyl (Aryl) Sulfonimide Zwitterions. Ph.D. Dissertation, Clemson University, Clemson, SC, 2006.

[12] Thampan, T.; Makhotra, S.; Zhang, J.; Datta R. PEM Fuel Cell as a Membrane Reactor. Catal. Today, **2001**, 67[1-3], 15-32,

[13] Vasquez, L. O., Fuel Cell Research Trends, Nova Publishers (2007) 34-65.

[14] Cheng, X.; Shi, Z.; Glass, N.; Zhang, L.; Song, D.; Liu, Z. S.; Wu, S.; Merida, W. A. A Review of PEM Hydrogen Fuel Cell. Journal of Power Sources. **2007**, 165, 739-756.

[15] Schmittinger, W.; Vahidi, A.; A Review of the Main Parameters Influencing Long-term Performance and Durability of PEM Fuel Cells. Journal of Power Sources. **2008**, 180[1], 1-14.

[16] Ticianelli, E. A.; Derouin, C. R.; Redondo, A.; Srinivasan, S. Methods to Advance Technology of Proton Exchange Membrane Fuel Cells. Journal of the Electrochemical Society. **1988**, 135, 2209.

[17] Barbir, F.; Braun, J.; Neutzler, J. Properties of Molded Graphite Bi-Polar Plates for PEM Fuel Cells. International Journal on New Materials for Electrochemical System. **1999**, 2, pp. 197–200.

[18] Uchida, M.; Fukuoka, Y.; Sugwara, Y.; Eda, N.; Ohta, A. Effects of Microstructure of Carbon Support in the Catalyst Layer on the Performance of Polymer-Electrolyte Fuel Cells. Journal of the Electrochemical Society. **1996**, 143 [11], 2545.

[19] Litster, S.; Mclean, G. PEM Fuel Cell Electrodes. J. Power Source. **2004**, 130, 61.

[20] Wilson, M.S.; Valerio, J.A.; Gottesfeld, S. Low Platinum Loading Electrode for Polymer Electrolyte Fuel Cells Fabricated Using Thermoplastic Ionomers. Electrochim. Acta. **1995**, 40[3], 355–363.

[21] Qi, Z.; Kaufman, A. Low Pt Loading High Performance Cathodes for Fuel Cells. J. Power Sources, **2003**,113, 37.

[22] Yu, Y.; Kosbach, L. Modified Carbon Products Useful in Gas Diffusion Electrodes. US6399202, **2002,** June 4.

[23] Jia, N.; Martin, R. B.; Qi, Z.; Lefebvre, M. C.; Pickup, P. G. Modification of Carbon Supported Catalysts to Improve Performance in Gas Diffusion Electrodes. Electrochimica Acta., **2001**, 46[18], 2863.

[24] Panchenko, A.; Dilger, H.; Moller, E.; Sixt, T.; Roduner, E. Insitu EPR investigation of Polymer Electrolyte Membrane Degradation in Fuel Cell Application. J. Power Sources **2004**, 127, 325-330, doi:10.1016/j.jpowsour.2003.09.047.

[25] Mauritz, K.A.; Moore, R.B. State of Understanding Nafion. Chem. Rev. **2004**, 104 4535.

[26] Yamaguchi, T.; Ibe, M.; Nair, B. N.; Nakao, S. A pore-filling electrolyte membrane Electrode Integrated System for a Direct Methanol Fuel Cell Application. J. Electrochem. Soc. **2002**, 149, A1448.

[27] Smitha, B.; Sridhar, S.; Khan. A. A. Solid Polymer Electrolyte Membrane for Fuel Cell. J. Mebran. Sci. **2005**, 259, 10.

[28] Fuel Cells 2000, Types of Fuel Cells. http;//www. Fuelcells.Org/fuel/fctypes.html (accessed Jan 2014).

[29] Chalkova E.; Fedkin, M. V.; Wesolowski., D. J.; Lvov, S. N. Effect of TiO_2 Surface Properties on Perfromance of Nafion-Based Composite Membranes in High Temoerature and Low Relative Humidity PEM Fuel Cell. J. Electrochem. Soc. **2005**, 152, A1742.

[30] Honma, I.; Nakajima, H.; Nishikawa, O.; Sugimoto, T.; Nomura, S. Family of High-Temperature Polymer-Electrolyte Membranes Synthesized From Amphiphilic Nanostructured Macromolecules, J. Electrochem. Soc., **2003**, 150, A616.

[31] Savadogo, O. Emerging Membranes for Electrochemical Systems. I. Solid Polymer Membranes for Fuel Cell Systems. J. New Mater. Electrochem. Syst. **1998**, 1, 47.

[32] Wilson, M. S.; Gottesfeld, S. Thin-Film Catalyst Layers for Polymer Electrolyte Fuel Cell Electrodes. J. Appl. Electrochem.**1992**, 22, 1.

[33] Creager, S. E. Proposal for DOE project, 2006.

[34] Kumar, G. S.; Raja, M.; Parthasarathy, S. High Performance Electrodes with Very Low Platinum Loading For Polymer Electrolyte Fuel Cells. Electrochim. Acta. **1995**, 40, 285.

[35] Cha, S.Y.; Lee, W. M. Performance of Proton Exchange Fuel Cell Electrodes by Direct Deposition of Ultrathin Platinum on the Membrane Surface. J. Electrochem. Soc. **1999**, 146, 4055.

[36] O'Hayre, R.; Lee, S. J.; Cha, S. W.; Prinz, F. B. A Sharp Peak in the Performance of Sputtered Platinum Fuel Cells at Ultra-Low Platinum Loading. J. Power Source. **2002**, 109, 483.

[37] Cohn, E. J.; Edsall, J. T. Proteins, Amino Acids and Peptides as Dipolar Ions, Rheinhold, New York, **1943**, 157.

[38] Laughin R. G. HLB from a Thermodynamic Perspective J. Soc. Cosmet. Chem. **1981**, 32, 371.

[39] Kirsch, P., Modern Fluoroorganic Chemisty: Synthesis, Reactivities, Applications Wiley-VCH: Weinheim, **2004**, pp182-223.

[40] Olah, G. A.; Iyer, P. S.; Prakash, G. K. S.Perfluorinated Resinsulfonic Acid (Nafion-Hw) Catalysis on Synthesis. Synthesis **1986**, 7, 513

[41] Koppe;, I. A.; Taft, R. W.; Anivia, F.; Zhu, S. Z.; Hu, L. Q.; Sun, K. S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Vlasoz, V. M.; Notario, R.; Maria, P. C. The Gas-Phase Acidities of Very Strong Neutral Bronsted Acids. J. Am. Chem. Soc. **1994**, 116, 3047.

[42] Harzdorf, C.; Meussdoerffer, J.; Niederprum, H.; Wechsberg, M. Uber Perfluoroalkanesulfinauren. Justus Liebigs Ann. Chem. **1973**, 33-39.

[43] Hampden-Smith, M. J.; Atanassova, P.; Napolitano, P.; Bhatia, Rice, G.I.; Caruso, J.; Brewster, J.; Gurau, B. Modified Carbon Products, Their Use in Fluid/Gas Diffusion Layers and Similar Devices and Methods Relating to the Same WO**2005**/091416, 2005.

[44] Isaacs, N. S. Physical Organic Chemistry, 2nd ed.; Wiley: New York, 1987; pp 335

[45] Kovačević, B.; Maksić, Z. B. Primorac, M. Acidity of Substituted Benzene-An Ab Initio Study of the Influence of Methoxy, Trifluoromethyl and Trifluoromethoxy Groups by a Novel Trichotomy Formula. Eur. J. Org. Chem. **2003**, 3777 −3783

[46] Mei, H.; D'Andrea, D.; Nguyen, T., Nworie, C. Synthesis of the Diazonium (perfluoroalkyl) benzenesulfonimide Monomer from Nafion Monomer for Proton Exchange Membrane. Journal of Power Source. **2014**, 248, 1177-1180

[47] Peter, A.; Smith, K; Comprehensive Organic Chemistry; The Synthesis and Reactions of Organic Compounds Sir Derek Barton, F., David Ollis, W., Eds.; Oxford: New York 1979: Vol 1, pp 122-123.

[48] Prasad, A. V.G.S.; Rameswara R.L.; Rao, P.V. One Pot Synthesis of Dibenzo [b,f][1,4]Thiazepine-11(10H)-One. ijCEPr, **2013**, 4 [1], 27-30

[49] Luche, J. L.; Bianc, C. Synthetic Organo Sonochemistry; Plenum Press: New York, 1998.

[50] Pasha, M . A., Jayashankara, V. P. Reduction of Arylnitro Compounds to Azoarenes and'/or arylamines by Al/NaOH in Methanol under Ultrasonic Conditions. Ultrason. Sonochem. **2005**, 12, 433-435.

[51] Shaw, R. The Chemistry of Diazonium and Diazo Groups, Patai, S., Eds.; John Wiley & Sons: New York; 1978; pp 199.

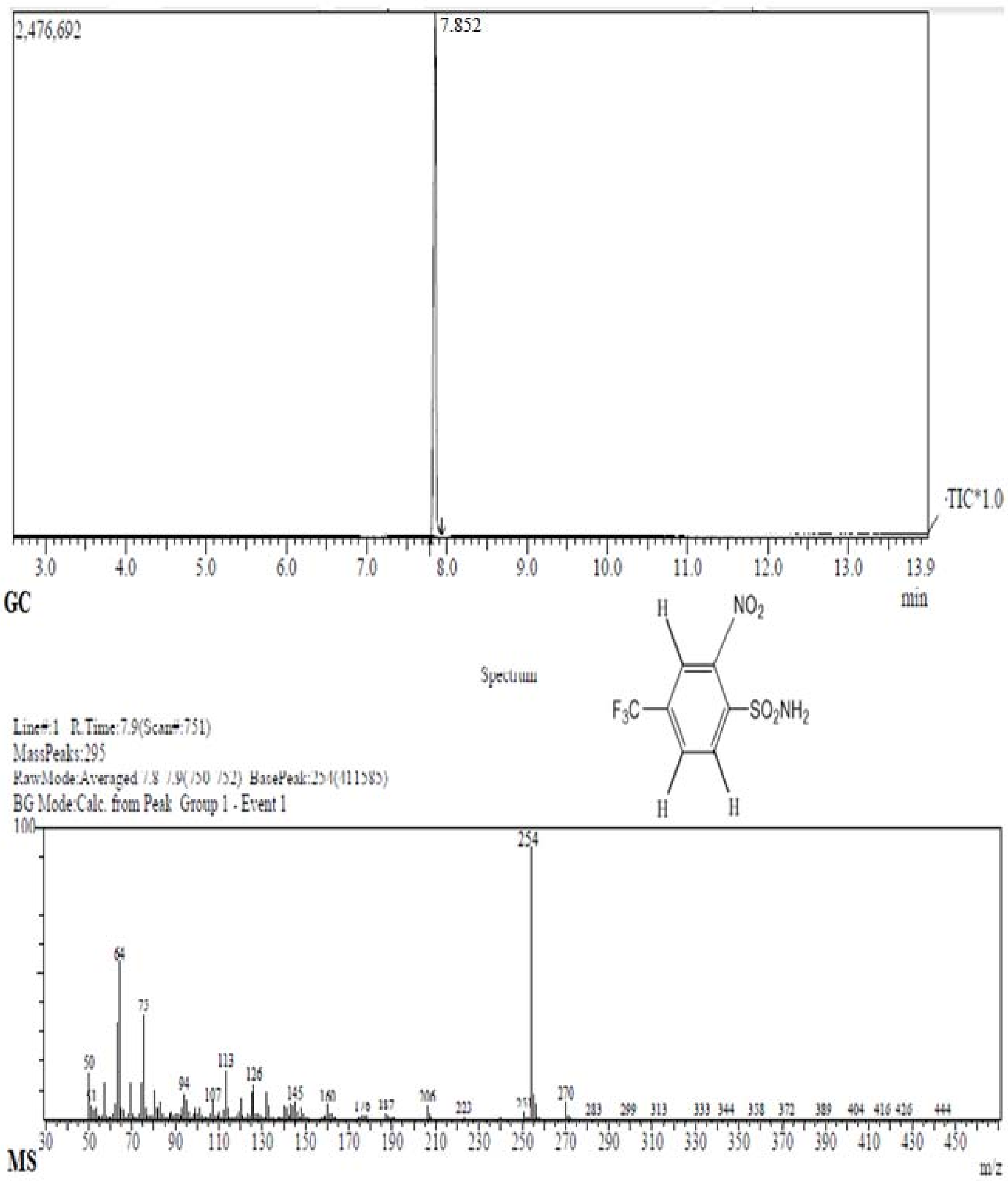
[52] Schank, K., Methodicum Chimicum, Kowski, F.Z., Eds.; Academic Press: New York, 1975; Vol. 6, pp 159.

[53] Greenwood, N. N., Earnshaw, A. Chemistry of the Element, 2nd ed., Oxford: Butterworth-Heineman; 1997. pp, 1231.

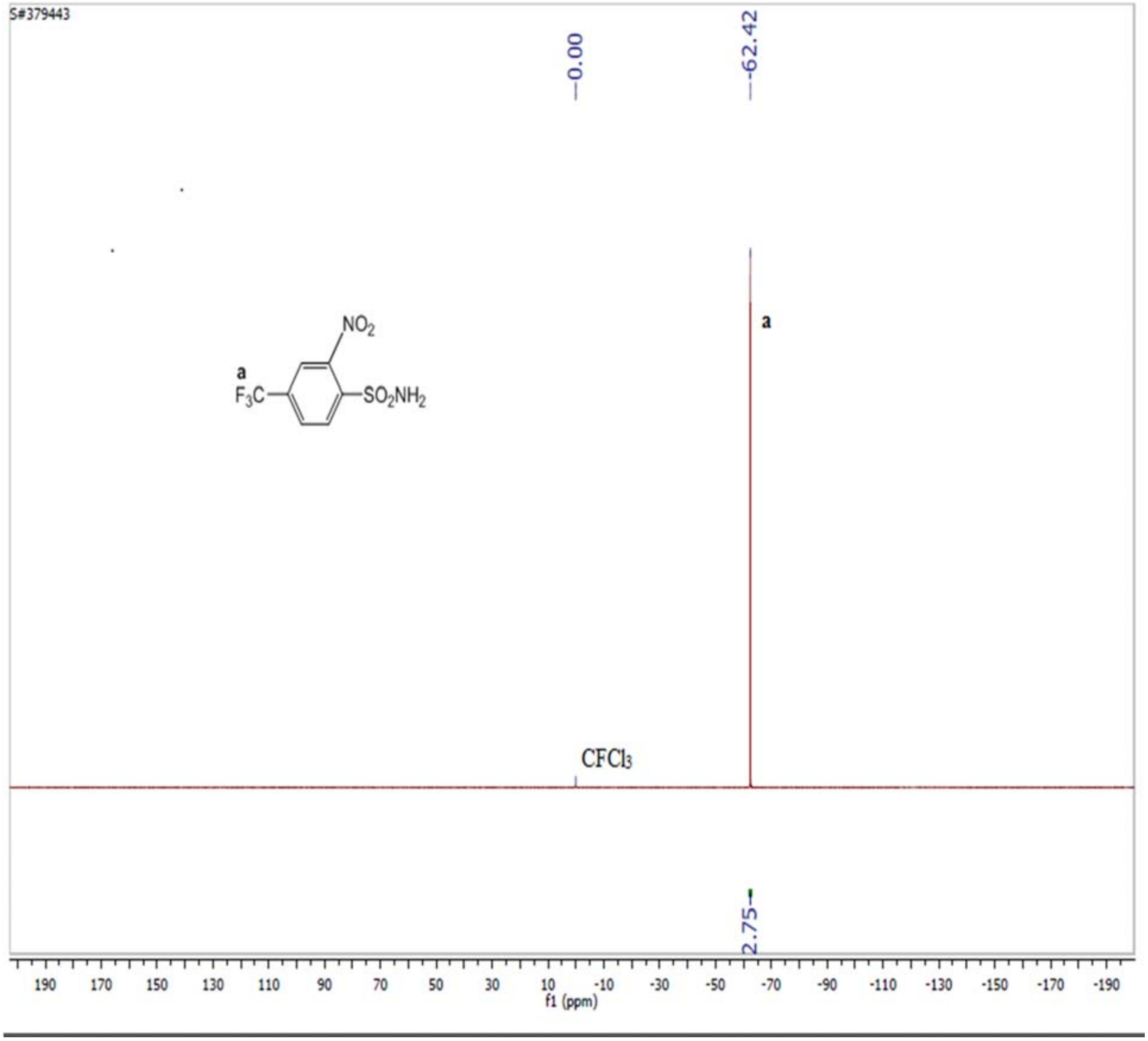
[54] Safety Emporium, www.ilpi.com/inorganic/glassware/vacline.html [accessed Jan 2014].

APPENDICES

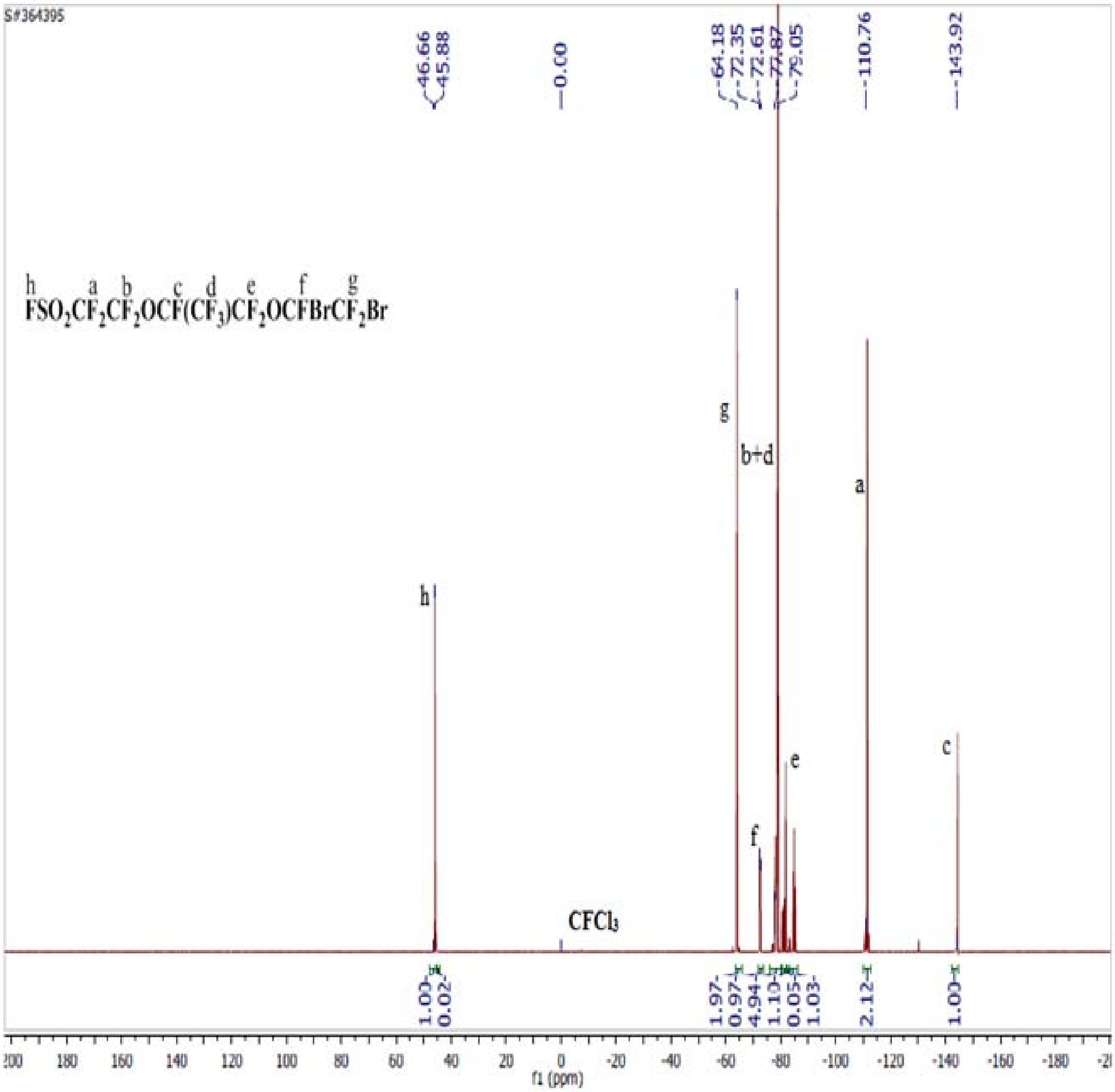
APPENDIX A: GC-MS Chromatogram of compound **2**



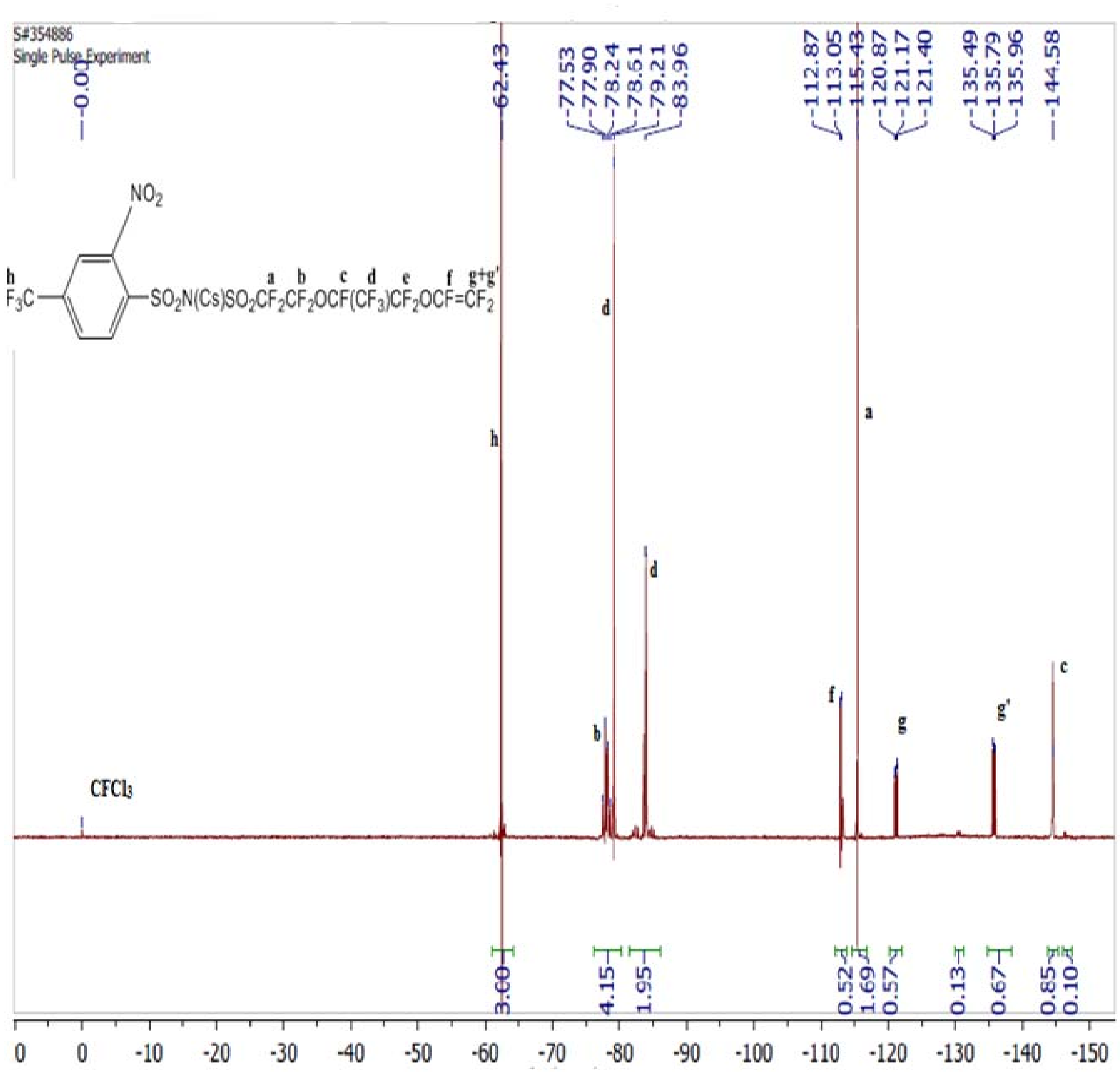
APPENDIX B1: ^{19}F NMR Spectrum of compound **2**, 400MHZ, CD_3CN



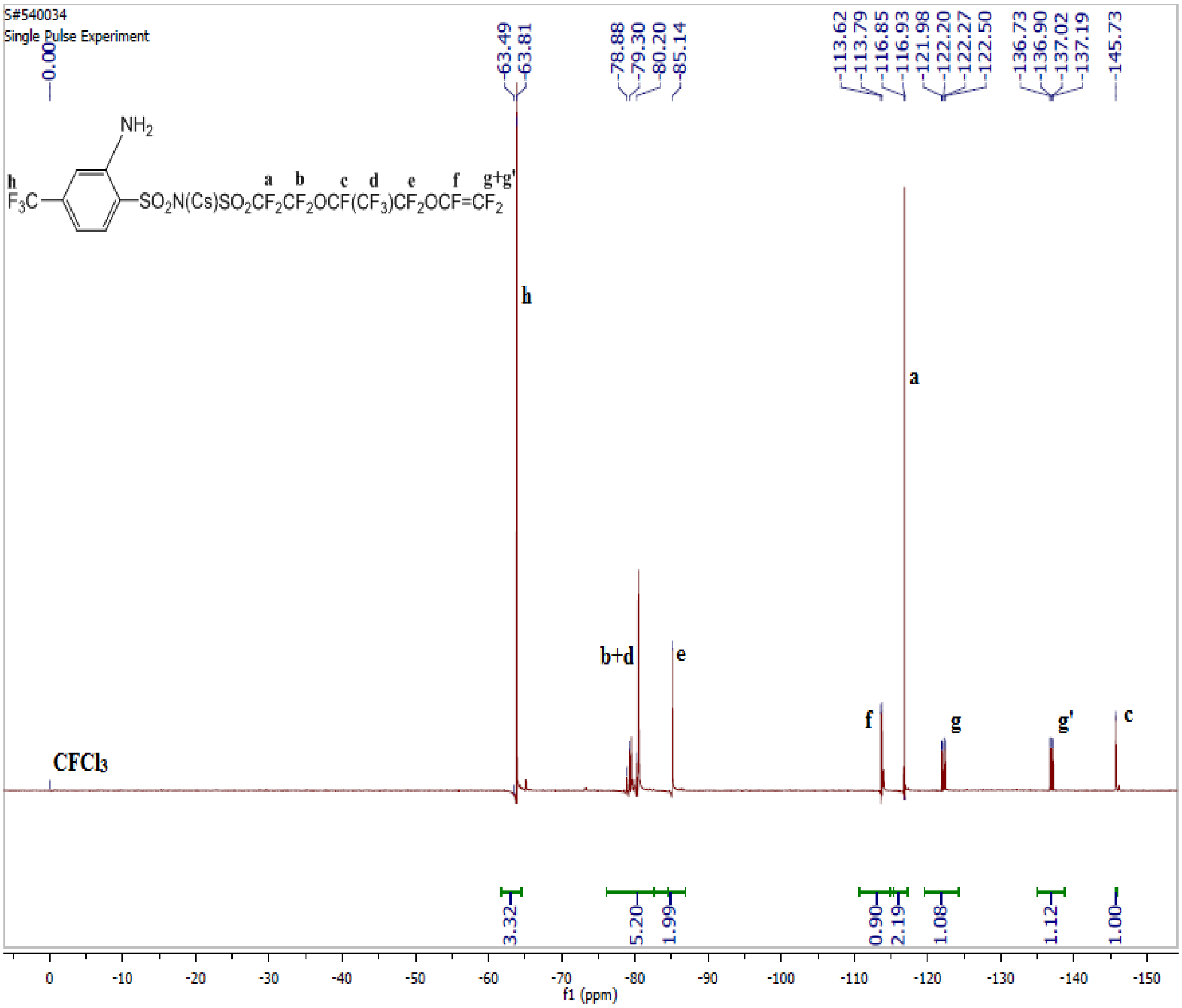
APPENDIX B2: ^{19}F NMR Spectrum of compound **4**, 400MHZ, CD_3CN



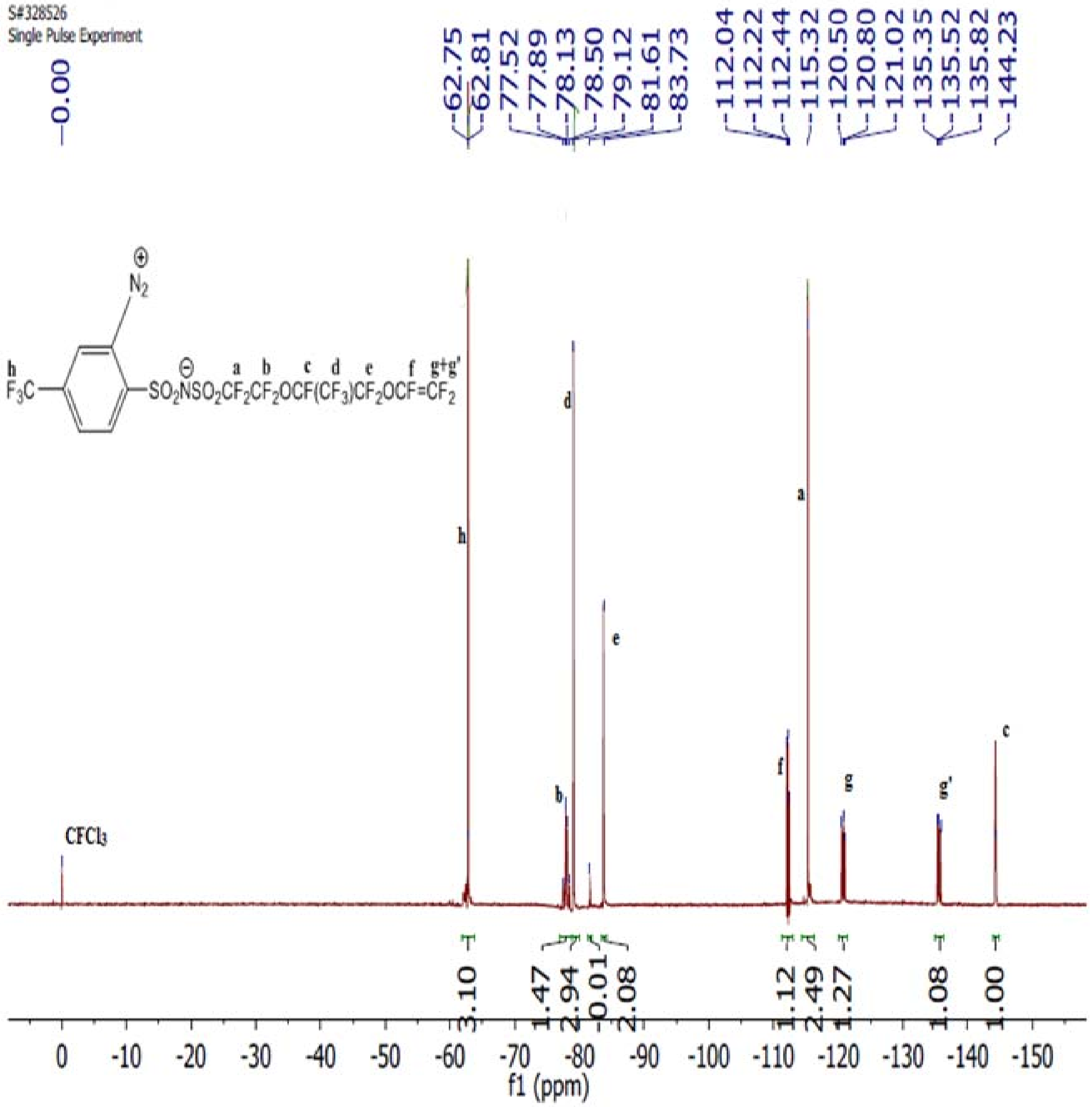
APPENDIX B3: ^{19}F NMR Spectrum of compound **5**, 400MHZ, CD_3CN



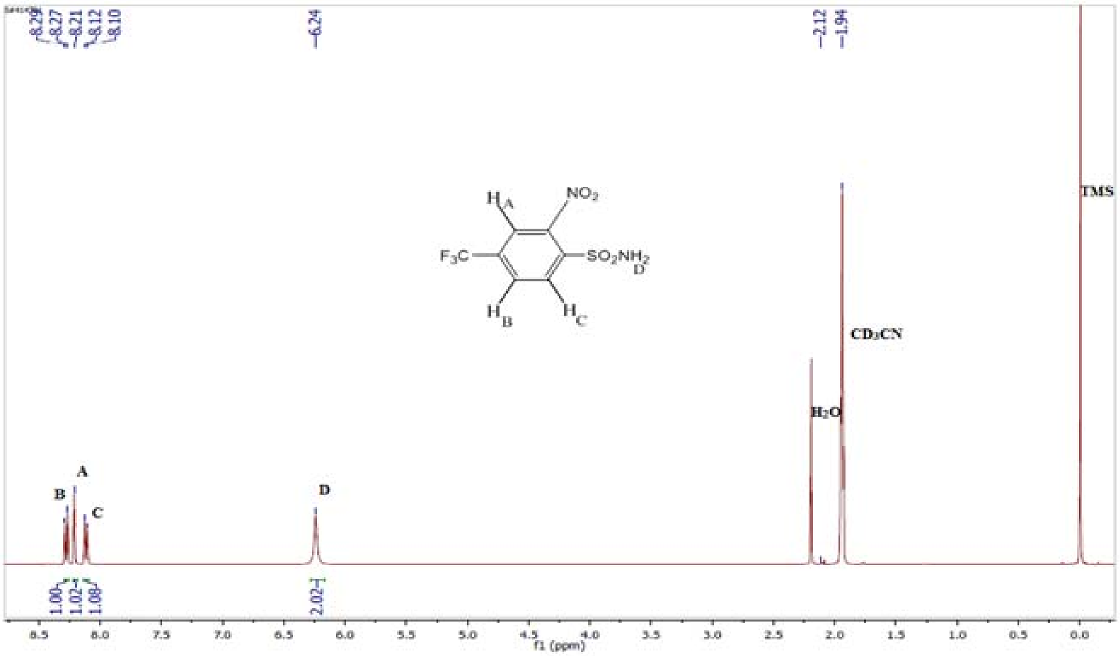
APPENDIX B4: ^{19}F NMR Spectrum of compound **7**, 400MHZ, CD_3CN



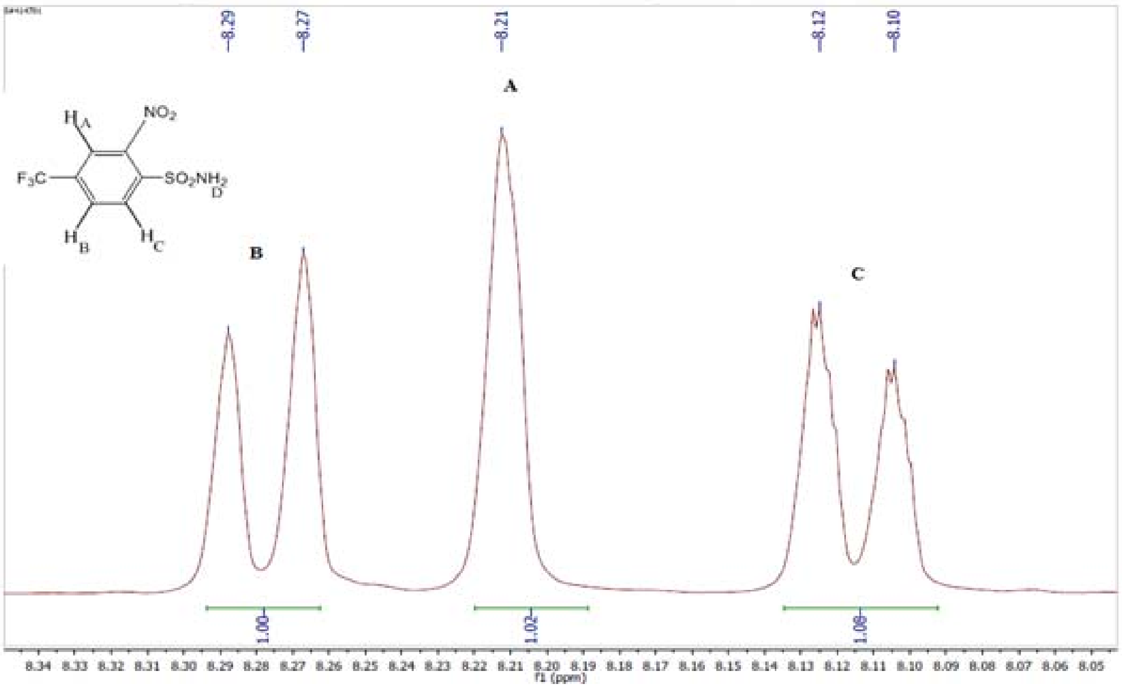
APPENDIX B5: ^{19}F NMR Spectrum of compound **8**, 400MHZ, CD$_3$CN



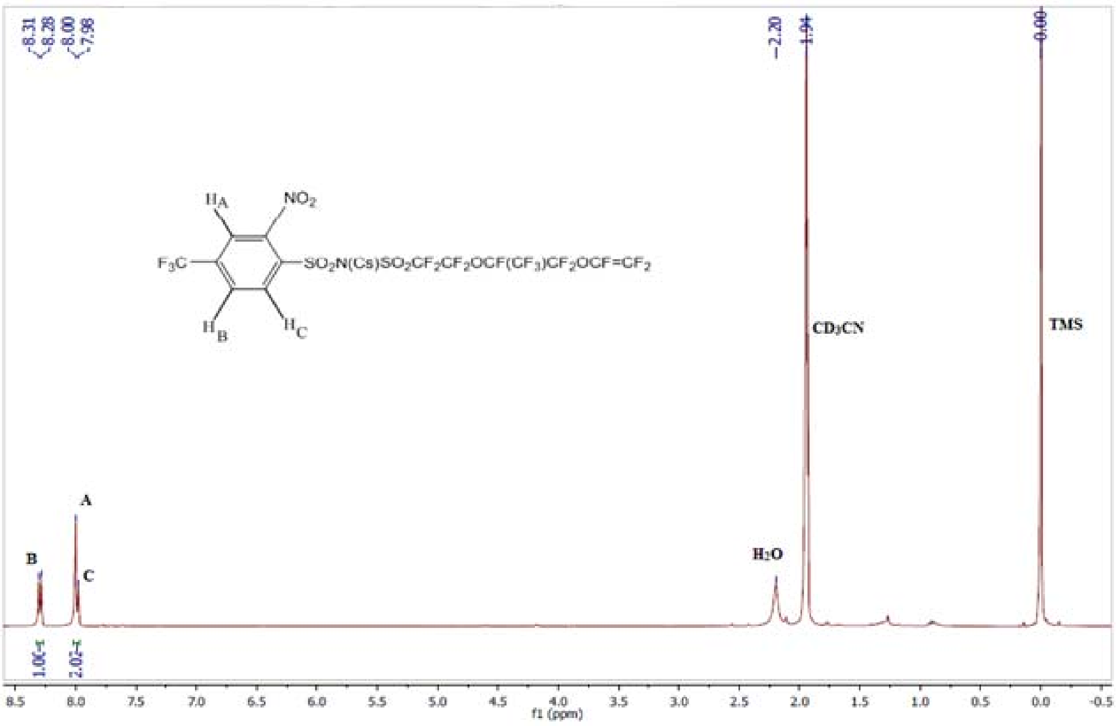
APPENDIX C1: ^{1}HNMR spectrum of compound **2**, 400MHz, CD_3CN



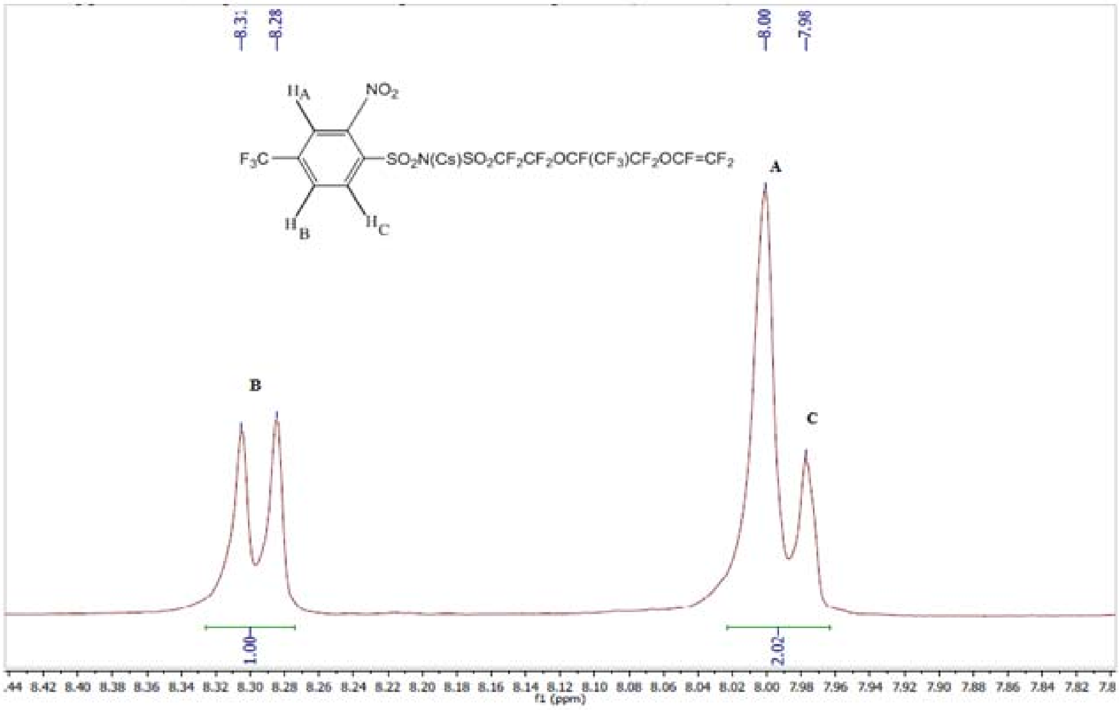
APPENDIX C2: Expanded ^{1}HNMR spectrum of compound **2**, 400MHz, CD_3CN



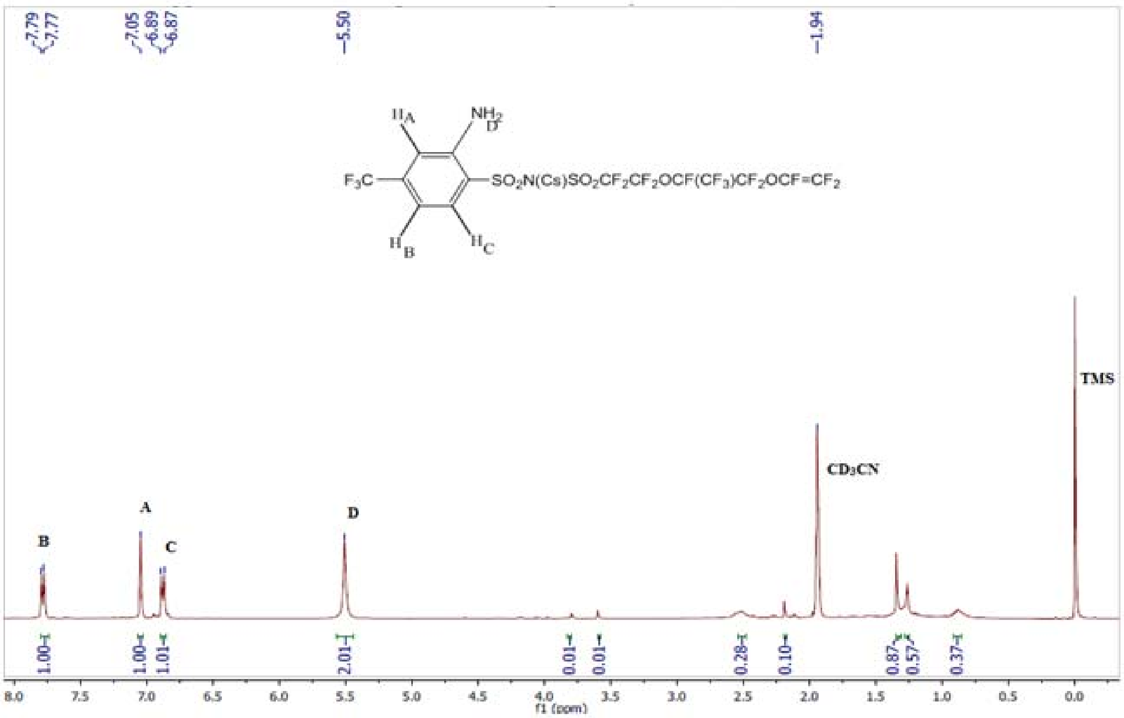
APPENDIX C3: ^{1}HNMR spectrum of compound **5**, 400MHz, CD_3CN



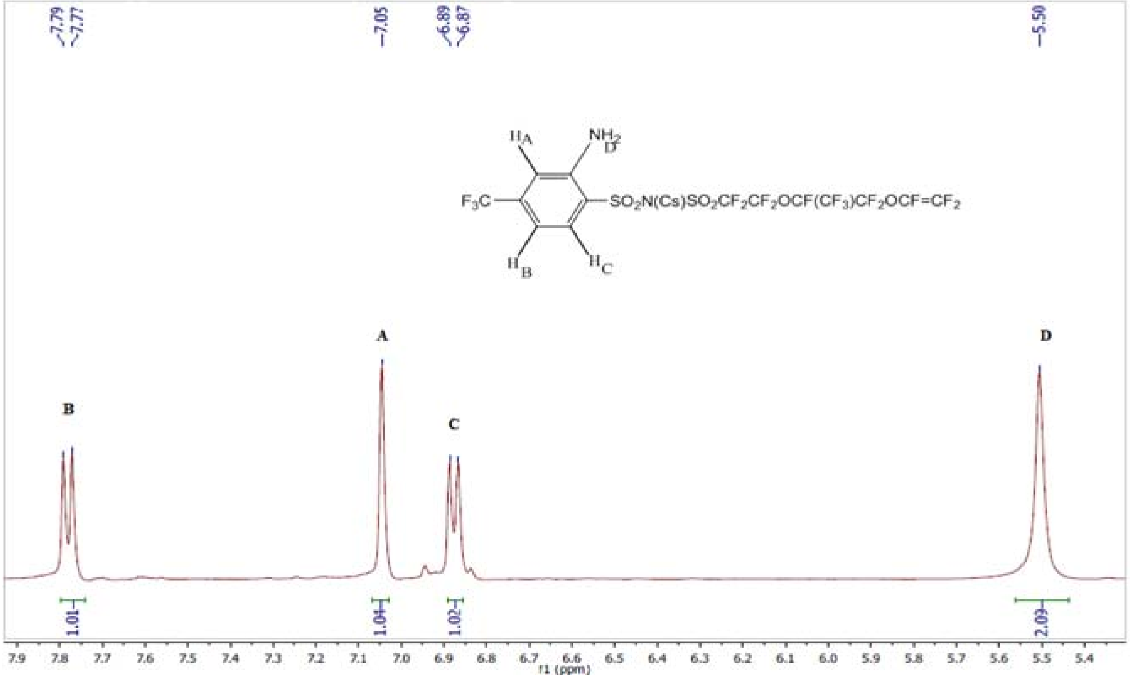
APPENDIX C4: Expanded ^{1}HNMR spectrum of compound **5**, 400MHz, CD_3CN



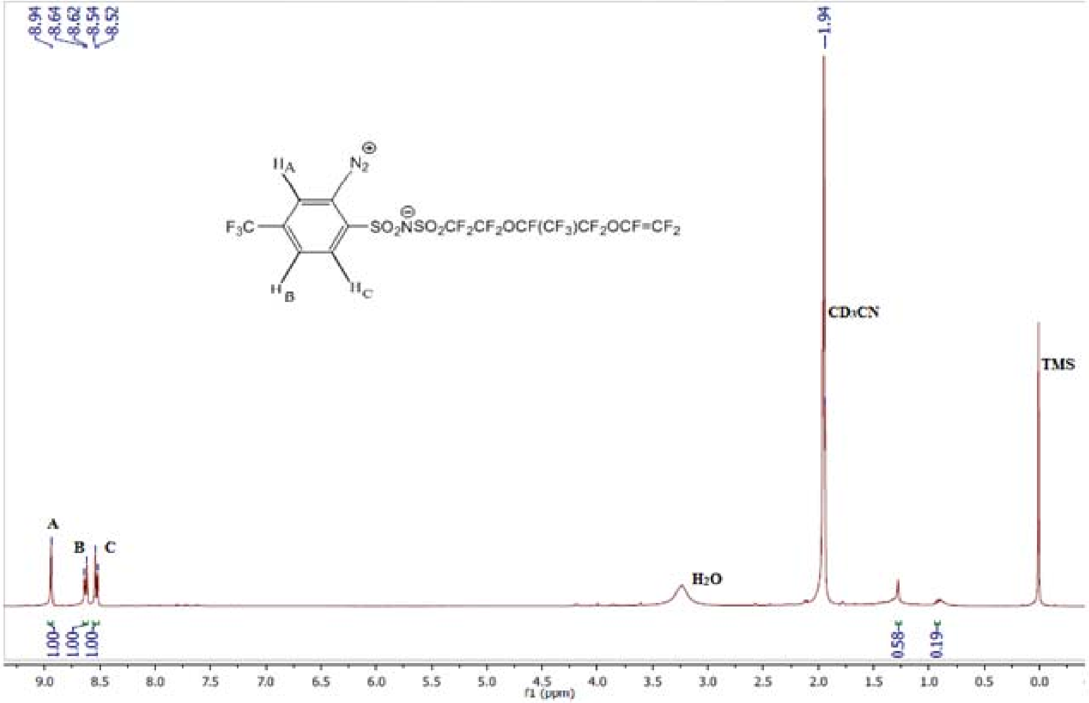
APPENDIX C5: ^{1}HNMR spectrum of compound **7**, 400MHz, CD_3CN



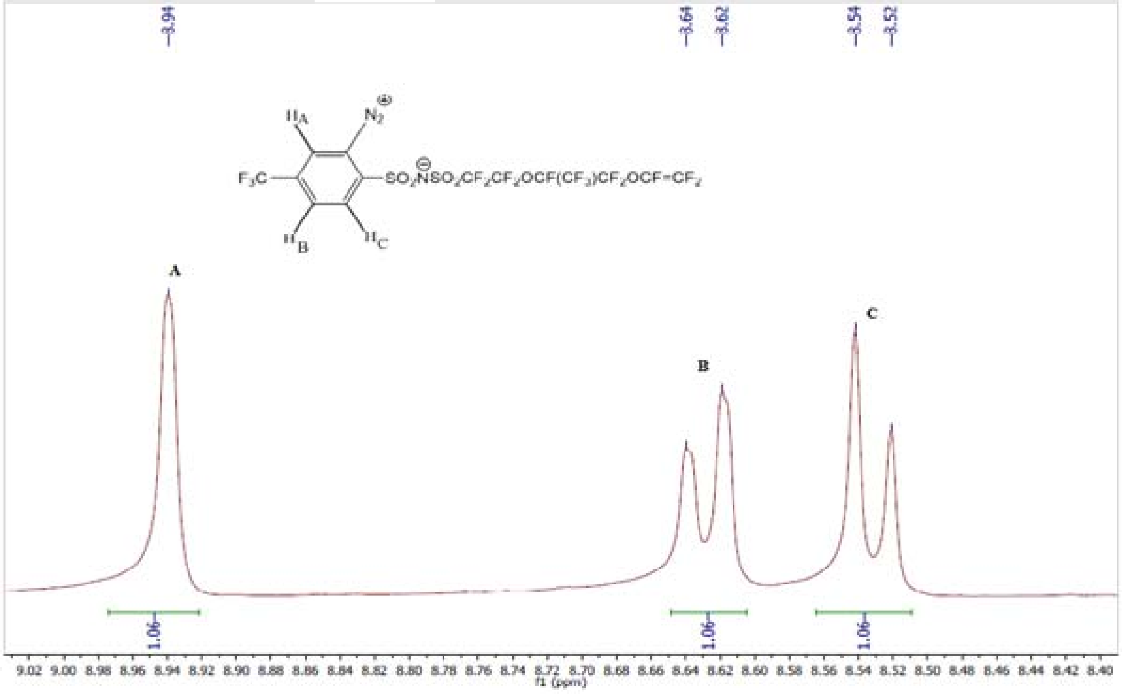
APPENDIX C6: Expanded ^{1}HNMR spectrum of compound **7**, 400MHz, CD_3CN



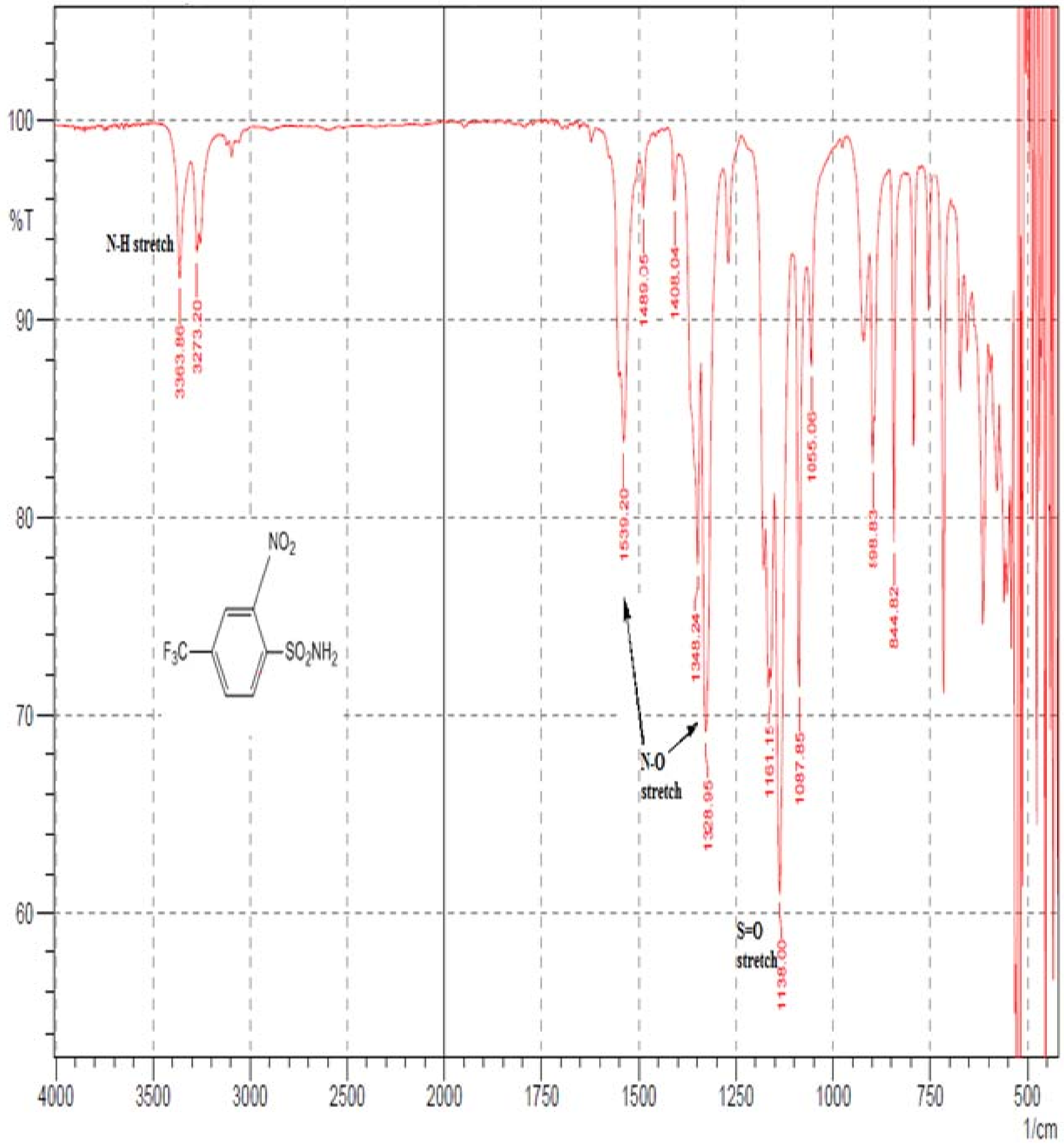
APPENDIX C7: ^{1}HNMR spectrum of compound **8**, 400MHz, CD_3CN



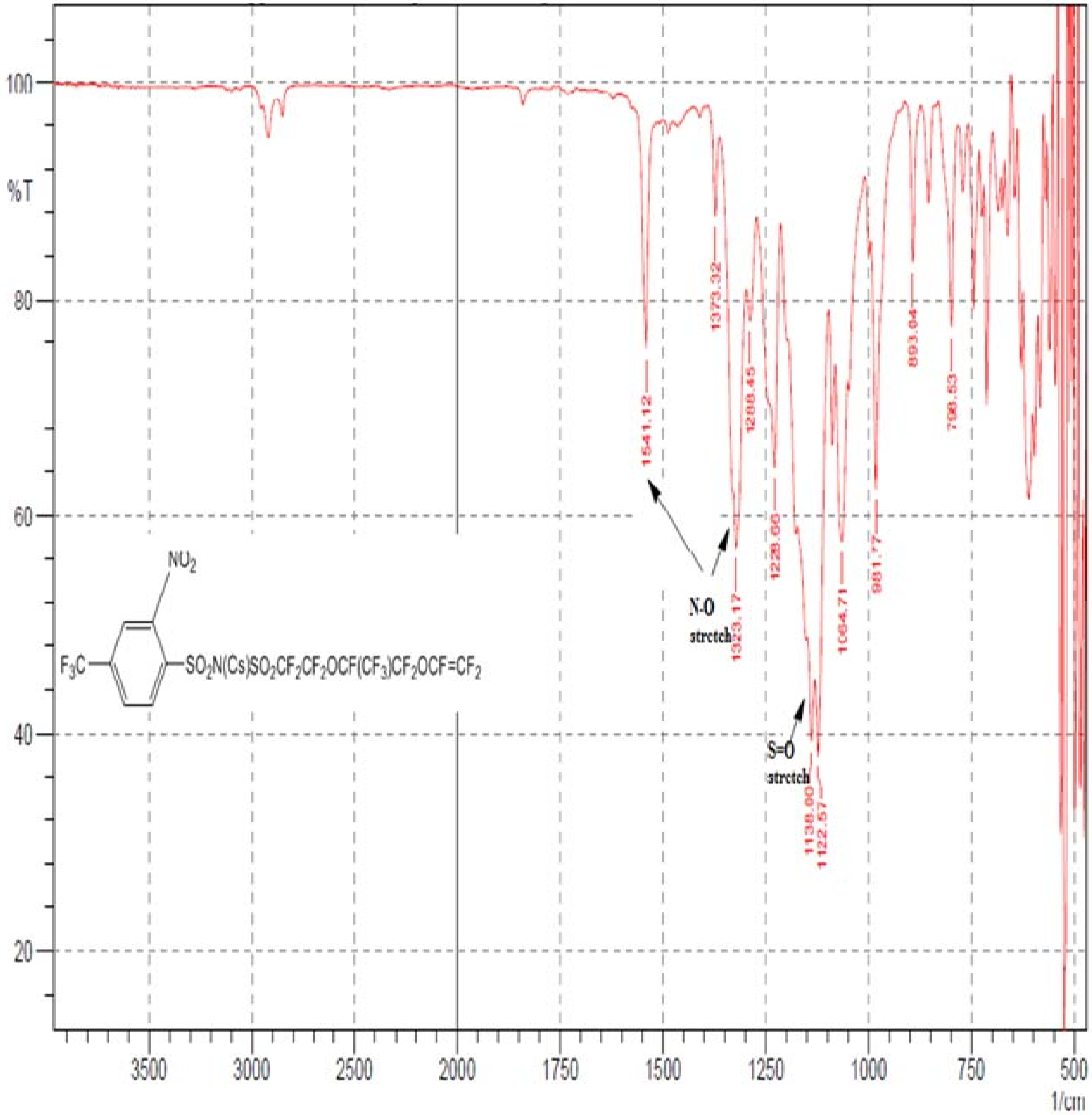
APPENDIX C8: Expanded ^{1}HNMR spectrum of compound **8**, 400MHz, CD_3CN



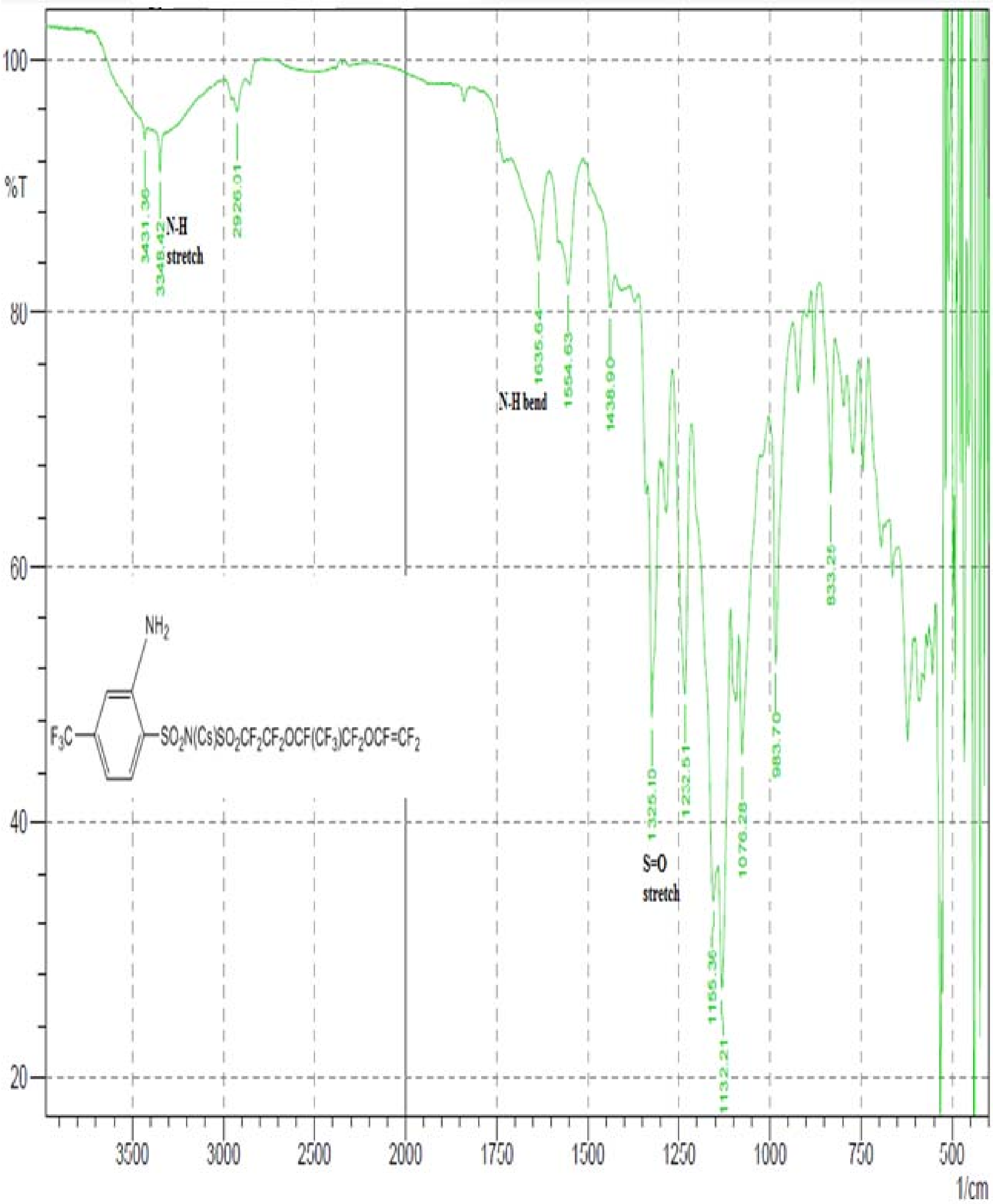
APPENDIX D1: FTIR spectrum of compound **2**



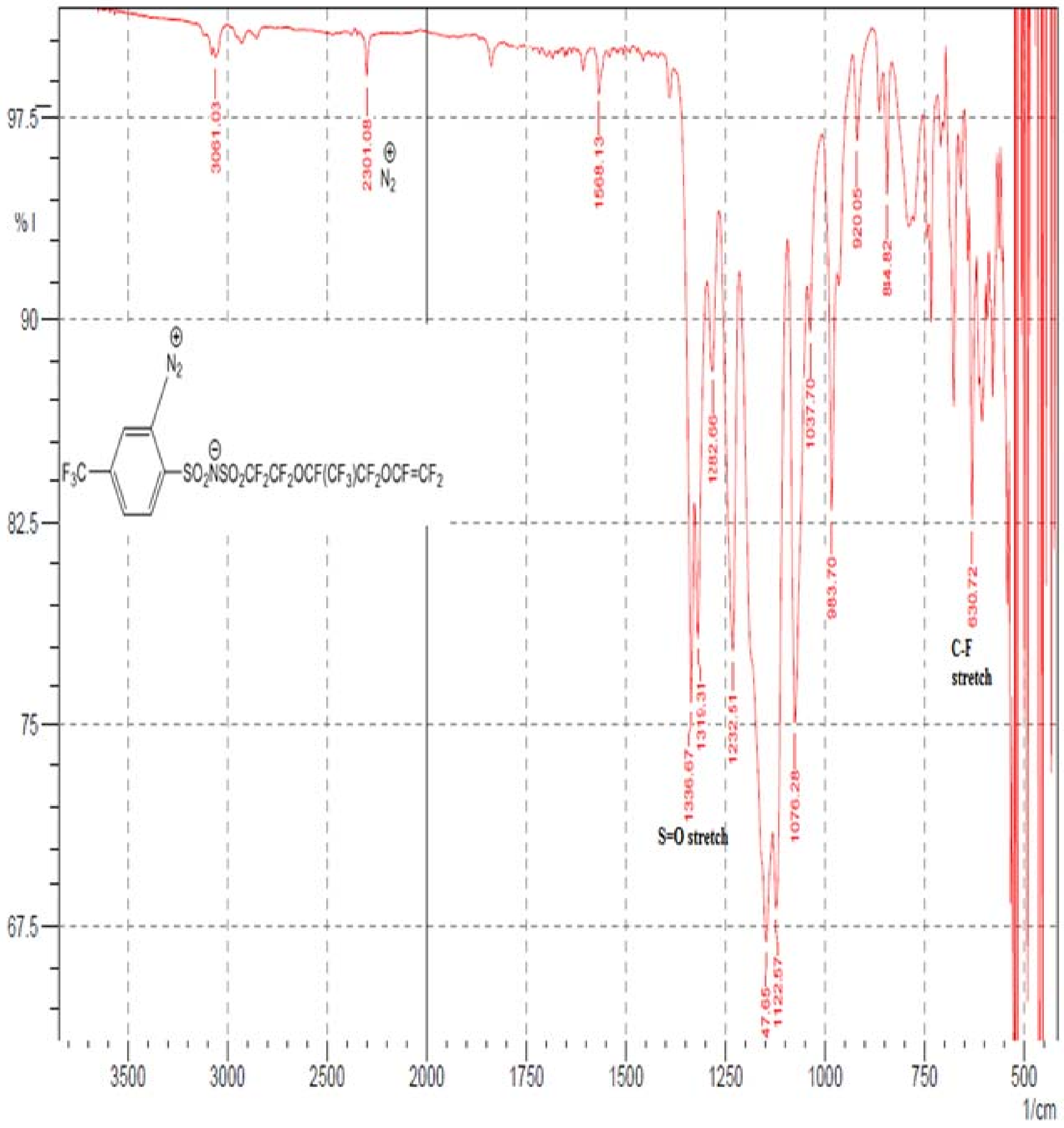
APPENDIX D2: FTIR spectrum of compound **5**



APPENDIX D3: FTIR spectrum of compound **7**



APPENDIX D4: FTIR spectrum of compound **8**



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