

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

A Convenient Way to Trap Toxic Elements in Water through Anionic Sensors *via* Polymer

Neelamegan Hari dharan*[#]

Department of Chemistry, National Institute of Technology Trichy, India[#]

ABSTRACT: Detection and recognition of anions such as fluoride, nitrate and chloride is an immense area of research interest to the scientific community due to its role in chemical, industrial, food and toxicity. We report a novel polymer based sensor which acts as an anion capsule for the detection of toxic anions present in water, which makes the water free from such kind of anions by simple binding. The sensor is prepared in such a manner that consists of a peculiar urea group on either end of the polymer. The anions binding are analyzed through monitoring with nuclear magnetic resonance spectroscopy which clearly shows the shift for various anions to the core of the sensor. The solid- state demonstration of anion guests by this versatile receptor could be useful in alkali-metal salt separation technology. Qualitative binding of salts of F⁻, Cl⁻, AcO⁻, and NO₃⁻ to the ligand used to understand the solution-state behavior of ligand in the presence of these anions. Disappearance of the amide -NH signal is observed immediately after the addition of Fluoride to the DMSO-d₆ solution of ligand. Furthermore, targeting the binding of contaminant anions from dilute solution must be combined with specific methods to remove or concentrate the resultant complexes contaminants from the remaining solution. Finally, the systems must be simple enough to scale for application on a large scale. Compared to small molecule, polymers chains with multiple recognition elements can increase both the binding efficiency and recognition selectivity for specific analyses.

KEYWORDS: amphiphilic, anionic sensors, toxicity, ligand, receptor.

I. INTRODUCTION

Anions play a major role in our daily life, being crucial to physiological function as well as various industrial processes.¹⁻⁴ Consequently in the environmental anionic species can be either essential to sustain that in the last decade. Detection and recognition of anions such as fluoride, nitrate and chloride is an immense area of research interest to the scientific community due to its role in chemical, industrial, food and toxicity. Many aquaculture production facilities operate as 'flow through' or 'open' systems thus releasing large quantities of nutrient rich water into another receiving body of water. At sufficiently high concentration levels, nutrient anions can become toxic to fish or lead to the crash of a phytoplankton bloom resulting in the rapid growth of filamentous algae or undesirable macrophytes.⁵⁻⁷ Productivity is the most conspicuous aspect of cultural eutrophication. It is accelerated by the runoff from aquaculture waste discharges, rich in nutrients.

The development of anionic sensors where the function, concentration and location of the negatively charged species can be monitored has become a very active area of research.⁸⁻¹⁰ The development of receptors for anions is of considerable interest in molecular recognition. Molecules containing functional groups such as amides, ureas/thioureas, guanidinium and ammonium derivatives can effectively bind anions using directional hydrogen bonding interactions and these types of compounds have widely been used for the binding of anions. But still the search of structurally simple receptor which can be easily synthesized and efficiently used has been of keen interest in the area of molecular recognition.

The usages of macromolecules in the host guest chemistry are of current interest due to its wide application range. Polymers have made a profound impact and have endowed modern sensory systems with superior performance. Polymers are widely used for the design of a range of receptors for charged or neutral molecules. Compared to small

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

molecule, polymers chains with multiple recognition elements can increase both the binding efficiency and recognition selectivity for specific analytes. There are several ways to detect pollutants in water with a polymer based sensor. Many works have been reported for the recognition of negatively charged species through the usage of

In the areas of aqueous waste treatment and environmental remediation, design of selective ligand systems for anions is complicated by additional factors. Highly specific ligands are needed that will bind a target species present in very low concentrations and in the presence of

much higher concentrations of other anions. Furthermore, binding of target contaminant anions from dilute solution must be combined with methods to remove or concentrate the resultant complexed contaminants from the remaining solution. Finally, the systems must be simple enough to scale for application on a large scale.

The incorporation of anionic receptors in to well defined polymers and other macromolecules is expected to produce materials that offer a number of advantages as compared to their small molecules analogues. Recently several articles have appeared that highlighted the importance of polymers based receptors for anionic species which will recognize that many anionic species such as fluoride, nitrate, phosphate and cyanide constitute major environmental pollutants. So the clear need for a material capable of recognizing, capturing and detecting those and other anionic species. Sessler et al., demonstrated a novel polymeric material with anionic receptors on the pendant side chains used as a chemosensor for species such as cyanide, fluoride and phosphate derivatives. Sessler and coworkers reported poly(methyl methacrylate) containing pendant calix pyrroles which are utilized for the extraction of fluoride and chloride from aqueous environment. Wang et al., reported a naked eye detection of anion binding of fluoride by using a polymer sensor based on hydroxyl functionalized polyquinoline derived macromolecule. Lee et al., tested a number of anions against polymer including chloride, sulphate and dihydrogen phosphate. Tian and coworkers developed a novel PPA containing naphthalimide subunits as a chemosensors for the successful detection of fluoride ions based on a unique intermolecular proton-transfer (IPT)

signaling mechanism. Swager et al successfully demonstrated a detailed review on the chemical sensor based on amplifying fluorescent conjugated polymers which can be advantageous for the selective detection of various metal ions. Valiyaveetil and coworkers reported a series of poly(*p*-phenylene carbazole) copolymers which contribute successfully for the colorimetric and fluorometric detection of iodide anions. Tian et al recently reported a review that deals the progress of polymers based fluorescent and colorimetric chemosensors for the successful detection of cation and anions. Miyata and Chujo reported a conjugated organoboron polymer which should be more sensitive to fluoride in chloroform due to fluoride coordination to boron. Wang reported that the phenolic derivative of polyquinoline could sense a 100- fold excess of fluoride through an amplified red-shifted fluorescence turn-on signal. Lee and co-workers reported a hydroxide sensing bipyridine based polymer linked with cyanostyryl groups. Ho and Leclerc reported that the colorimetric and fluorometric detection of iodide using a cationic poly(3-alkoxy-4-methylthiophene).

Stimuli responsive polymers that can change their volumes drastically in response to various external physical and chemical stimuli have been of much interest. Recently, polyethylene glycol (PEG) and its aqueous solutions represent interesting solvent systems for solvent replacement, and may stand comparison to other currently favored systems such as ionic liquids, supercritical carbon dioxide and micellar systems. PEG's are selected instead of other polymers because they are inexpensive, biodegradable, non-halogenated and having low toxicity.

The polyethylene glycol (PEG) is considered to be water soluble, but after specific modifications it acts as a both hydrophilic and hydrophobic moiety to improve the permeability of ions in to the polymer recognition group. Separation of soluble polymers (with bound anions) from solution can be accomplished with molecular sieving techniques such as ultra filtration which has been demonstrated for a wide molecular weight range of functional metal binding polymers.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

II. EXPERIMENTAL SECTION

Materials

Polyethylene glycol 1500, Phenyl isocyanate, deuterated chloroform (CDCl_3) and deuterated dimethyl sulfoxide (DMSO *d*6) were purchased from Aldrich and used as received without further purification. Tetrabutylammonium chloride (TBACl), tetrabutylammonium fluoride (TBAF), tetrabutylammonium nitrate (TBAN) and tetrabutylammonium acetate (TBAAc) were purchased from Alfa Aesar chemicals and used as received. Dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were purchased from Aldrich and SRL chemicals and distilled, before use wherever applicable.

Instrumentation

^1H NMR spectra were recorded on a Bruker 500 MHz spectrometer. For NMR, DMSO *d*6 and CDCl_3 were used as solvents, TMS as internal standard. IR spectra were recorded with a JASCO FT/IR-460 plus spectrometer, using KBr discs. The mass spectrum was performed using a GC-MS mass spectrometer (WATERS) with electrospray ionization.

Synthesis of butyl -1-cyanoethylcarbonotrithioate

A 250 ml 3-neck round bottom (RB) flask (fitted with septum and reflux condenser with N_2 bubbler) was charged with Poly(ethylene glycol) bis(3-aminopropyl) terminated in 15 ml of dimethyl formamide. The temperature of the mixture was maintained between 0 and 5 °C. Phenylisocyanate was added over 10 min to the RB flask and the mixture was stirred for 6 hrs. After the mentioned time period, the reaction mixture was filtered, washed with dichloromethane twice. The crude product of butyl -1-cyanoethylcarbonotrithioate as a yellow color solid.

Yield of CTA: 85%

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 4.9 (q, 1H, -S-CH carbon), 3.4 (t, 2H, -SCH₂ carbon), 1.8 (d, 3H, -SCH₃ carbon), 1.7 (quintet, 2H, -CH₂ carbon), 1.45 (sextet, 2H, -CH₂ carbon), 0.95 (t, 3H, -CH₃ carbon). ^{13}C NMR (100 MHz, CDCl_3 , δ , ppm): 219.8 (C=S), 119.0 (C=N), 37.5 (S-CH₂), 32.0 (CH₂ carbon), 22.0 (-CH₂ carbon), 16.0 (S-C(CH₃) carbon), 13.0 (-CH₃) carbon).

III. RESULTS AND DISCUSSION

Due to the wide familiarity of the anion recognition, the design of synthetic receptors still remains a great challenge due to their larger size than cations, and the effects of other variables like their chemical environments and the pH of the medium on the behavior of anions. Due to larger size and higher charge density, they remain highly solvated in polar protic solvent e.g. H_2O . Therefore recognition of anions in water is really a challenging work. Herein we report simple polyethylene glycol based colorimetric receptors for the selective recognition of anions such as fluoride, nitrate, chloride and acetate. This novel sensor is prepared by reacting poly(ethylene glycol) with phenyl isocyanate in DMF medium at lower temperature. The detailed synthetic procedure and characterization data are given in the experimental data. The ^1H NMR spectra of the obtained sensor in DMSO *d*6 shows five prominent peaks at 8.63, 7.44, 7.28, 6.95 and 3.48 ppm respectively. These peaks corresponds to protons from the -NH, -CH, -(CH₂)_n groups and confirm the structure of the sensor. The GC-MS mass spectrum of the sensor (shown in the Supporting Information Fig) provide additional evidence for the structure. The nature of the synthesized sensor are deviated from completely water soluble nature wherein it behaves both as a hydrophobic and hydrophilic. Since poly(ethylene glycol) is covalently binded to phenyl isocyanate it should enhance the property of efficacy. Further the synthesized sensor is non-toxic in nature and hence it is more suitable for aquatic environment. Therefore the synthesized sensor is more suitable for anion recognition which also possesses a reorganized bipedal cleft with amide NH protons suitable for the recognition.

Solution-State Anion Binding Studies.

Qualitative ^1H NMR experiments were performed with tetrabutylammonium salts of F^- , Cl^- , Br^- , AcO^- , NO_3^- and phosphate to understand the solution-state behavior of the sensor (figs 1 and 2) in the presence of these anions. The addition of the sensor to the solution of tetrabutylammonium fluoride in DMSO-*d*6 results in a downfield shift of 1.22 ppm for the free fluoride resonance, indicating the participation of the anion in hydrogen bonding with -NH of the

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

receptor. The anions prefer to bind with the $-NH$ group rather than $-CH$ group as shown in fig.3 . Similar solution-state binding was also observed in case of the sensor with tetrabutylammonium bromide in $DMSO-d_6$. However only a slight shift of 0.05 ppm is observed from the free polymer indicating that binding affinity of the polymer to the bromide is not efficient compared to fluoride as shown in fig.4 Similarly in case of the sensor with AcO^- in $DMSO-d_6$, it shows no appreciable change in chemical shift (fig.5). However upon addition of NO_3^- to the sensor, a very slight (0.02 ppm) change in chemical shift was observed. Solution-state binding studies of phosphate shows a shift of 0.24 ppm from the free polymer compared to AcO^- , NO_3^- and Br^- indicating that the polymer has an affinity to bind with phosphate.

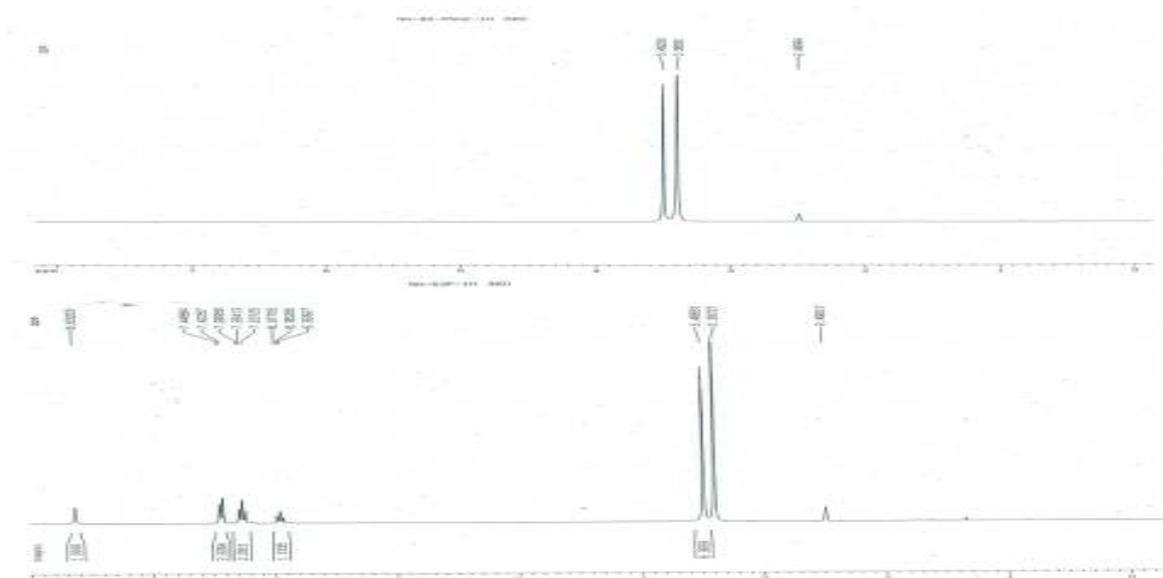


Fig.1 1H NMR Spectrum of the polymer based sensor.

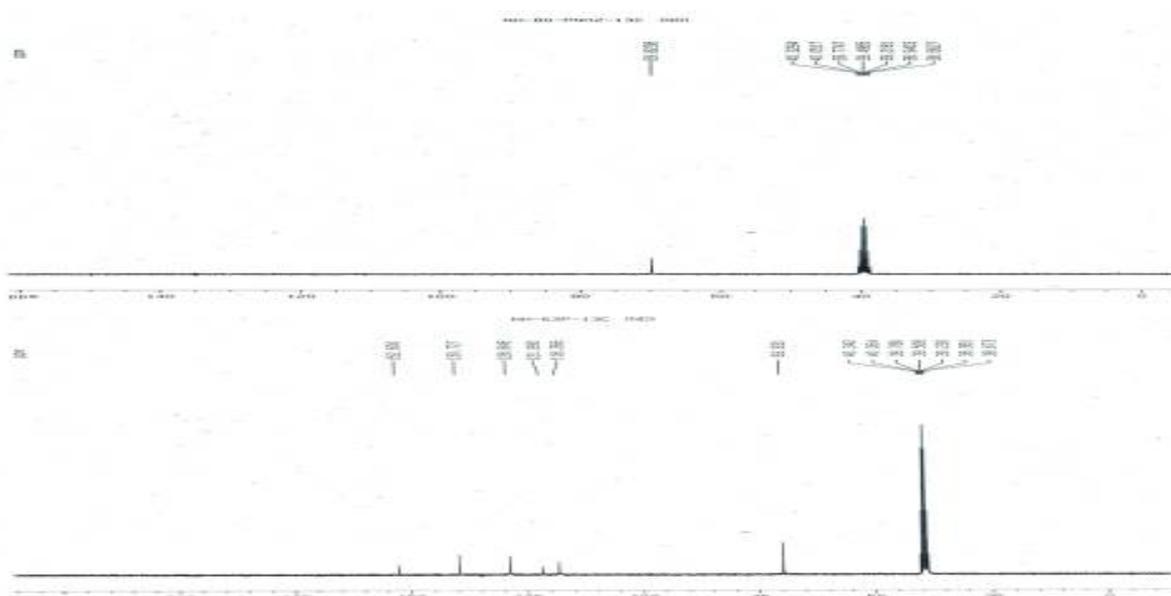


Fig.2 ^{13}C NMR Spectrum of the polymer based sensor.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

When the sensor is added to the solution of tetrabutylammonium chloride in DMSO-*d*₆ results in a downfield shift of 0.83 ppm for the free chloride resonance and its binding affinity is much higher compared to phosphate, indicating the superior participation of the chloride in hydrogen bonding with -NH of the receptor but less than that of fluoride.

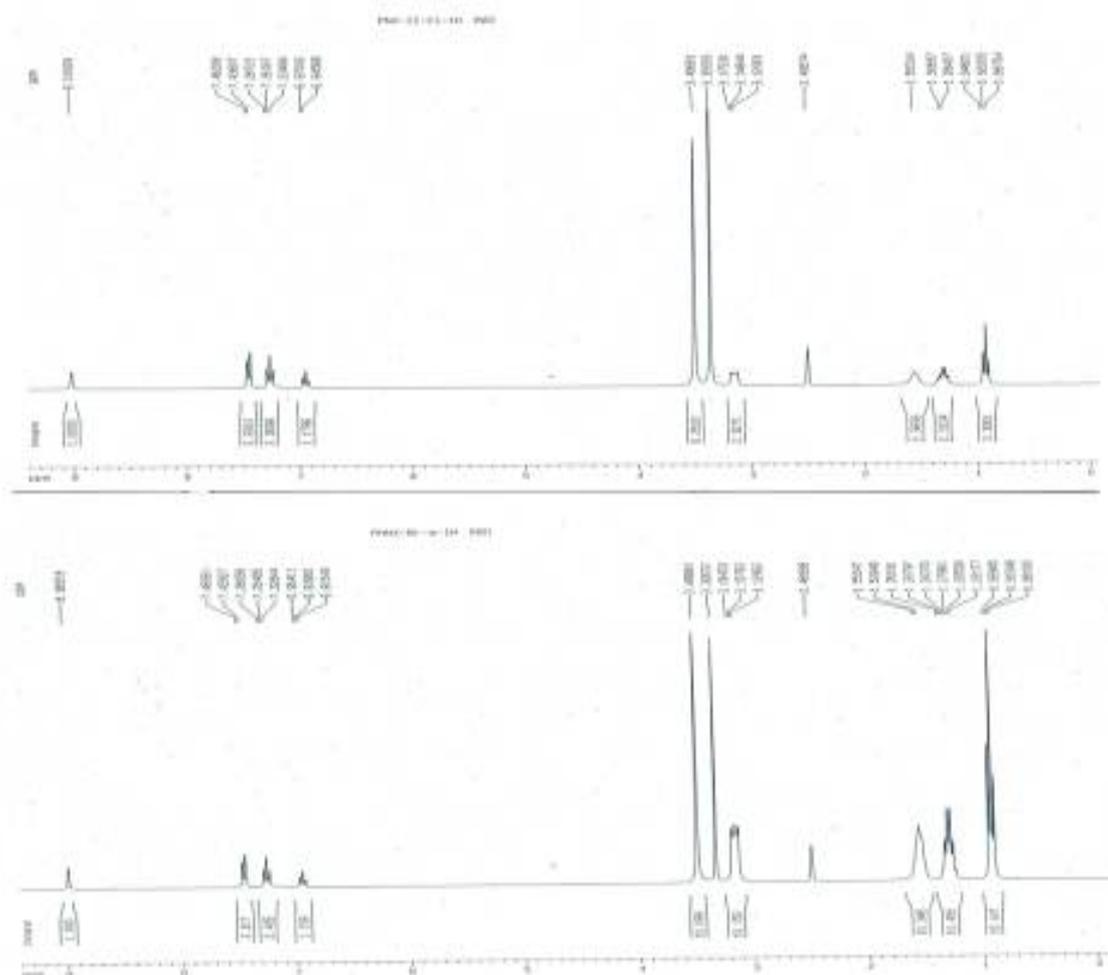


Fig. 3 ¹H NMR Spectrum depicts the binding of bromide to the sensor

A greater downfield shift in the NH proton signal was observed upon exposure to TBAF over TBACl. These results are consistent with the ability of polymer to extract fluoride over chloride and bromide. The increased steric hinderance also has an effect on the solution phase binding. These results illustrate that the halide with smaller atomic size bind effectively with the polymer. The sensor binds F⁻ too strongly which can be measured by means of ¹H NMR methods.

The chloride also observes similar result but less effectively than fluoride. This result illustrates that halides has better binding affinity to sensors compared to other anions. The selective trend of anion binding to polymer is F⁻ > Cl⁻ > PO³⁻ > Br⁻ > NO³⁻ > AcO⁻ Rambo *et al.*, illustrated that

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

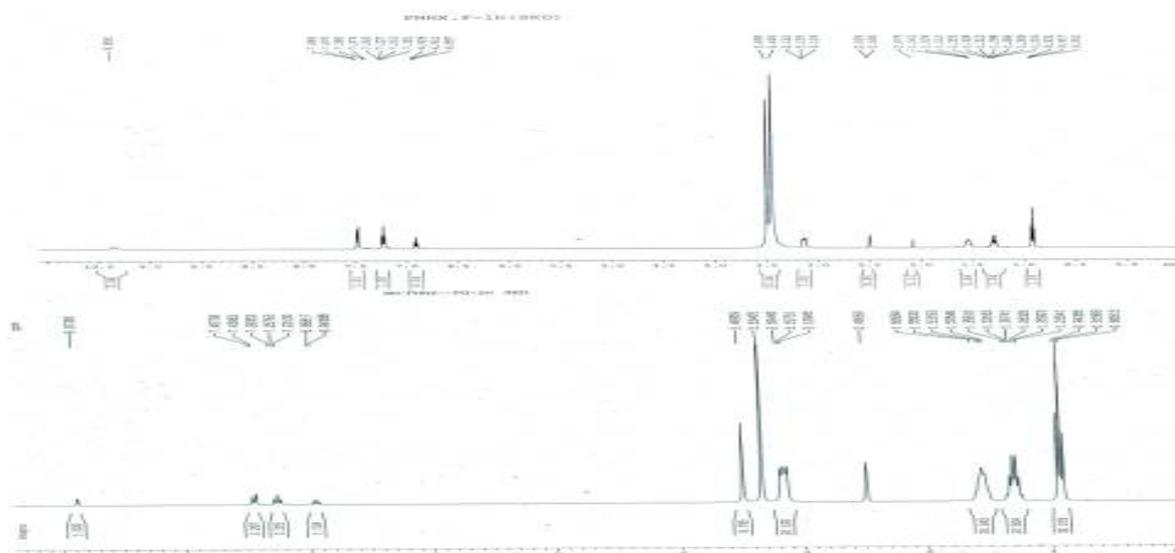


Fig.4 ¹H NMR Spectrum depicts the binding of fluorine to the sensor

PMMA were capable of extracting TBACl, but 35 % less efficiently than urea based polymer systems. In the case of TBAF only urea based polymers was capable of removing fluoride from the aqueous layer but not with methacrylate system.

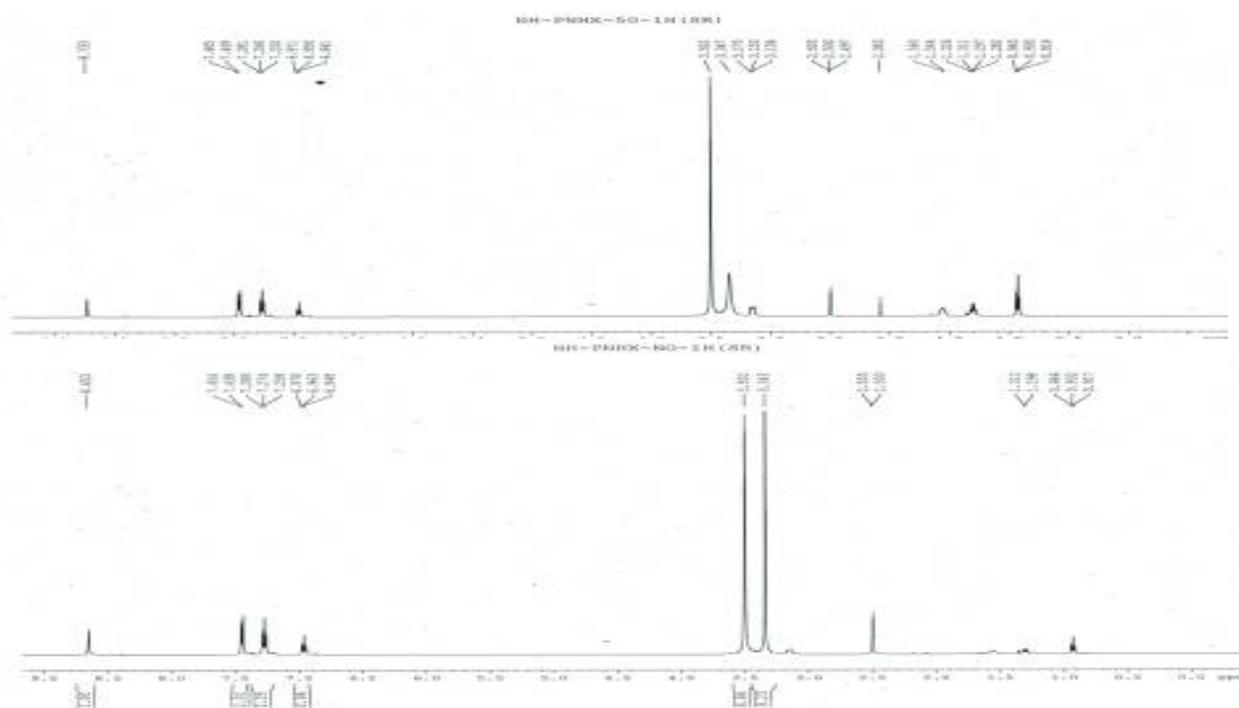


Fig.5 ¹H NMR Spectrum depicts the binding of acetate to the sensor

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

It is well known that the macromolecules containing hydrophobicity and hydrophilicity species can be tuned and was expected to be characteristic of the material. The use of appropriate solvents leads to swelling or shrinking of the films, which should result in absorption of the anions from the system. The sensor which can be made from poly (ethylene glycol) with phenyl isocyanate acts as an amphiphilic which can be utilized sufficiently for the binding of the anions where the hydrophobic core contains the binding site and the hydrophilic core contains the polyethylene glycol units. The polymer swells in water and effectively catches the anions like fishing. The polymer was colorless in solution; however, upon addition of fluoride salts, a change to deep blue color was observed. Similarly, upon addition of chloride salts, a change to dark yellow was observed which clearly monitors the binding affinity of the polymer to different anions in solution state. However, the nature of the acetate and nitrate counter anion was found to have no influence on the observed color change.

IV. CONCLUSION

In this manuscript, I report a simple way of synthesizing anionic sensor for tracing toxic elements such as nitrate, acetate, fluoride and chloride etc., The anionic sensor prepared through polyethylene glycol which should considered being eco-friendly by reacting it with phenyl isocyanate in a DMF medium without the necessity of any catalyst. The synthesized anionic sensor is also confirmed through NMR and mass spectroscopic techniques. The synthesized polyethylene glycol based sensor acts like an amphiphilic moiety that could be used for tracing anions and can be monitored through proton NMR spectroscopy. This method paves the way for the efficient removal of toxic elements from water through eco-friendly media which is more helpful to the environment and also to reduce water pollution.

REFERENCES

1. Bianchi, A.; Bowman-James, K.; García-España, E., Eds. *Supra-molecular Chemistry of Anions*; Wiley-VCH: New York, 1997.
2. Gale, P. A.; García-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.* 2008, 37, 151–190.
3. Kang, S. O.; Powell, D.; Day, V. W.; Bowman-James, K. *Angew. Chem., Int. Ed.* 2006, 45, 1921–1925.
4. Brooks, V. S. J.; García-Garrido, S. E.; Light, M. E.; Cole, P. A.; Gale, P. A. *Chem. Eur.* 2007, 13, 2564.
5. Dujols, V; Ford F, Czarnik AW. *J. Am. Chem. Soc.* 1997, 119(31), 7386-7387.
6. Yoosaf, K; Ipe, B; Suresh, C.H; Thomas, K.G. *J. Phy. Chem. C.* 2007, 111(34), 12839-47.
7. Gunnlaugsson, T; Leonard, J. P.; Murray, N.S.; 2004, 6(10), 1557-60.
8. Lee, M.H.; Cho, B.K.; Yoon, J.; Kim, J.S; *Org. Lett.* 2007, 9(22), 4515-4518.
9. Mu, H.; Gong, R.; Ma, Q.; Sun, Y; Fu, E. *Tetrahedron Lett.* 2007, 48(31), 5525-9.
10. Lim, M.H.; Lippard, S. *Acc. Chem. Res.* 2007, 40(1), 41-51.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

Supporting Information

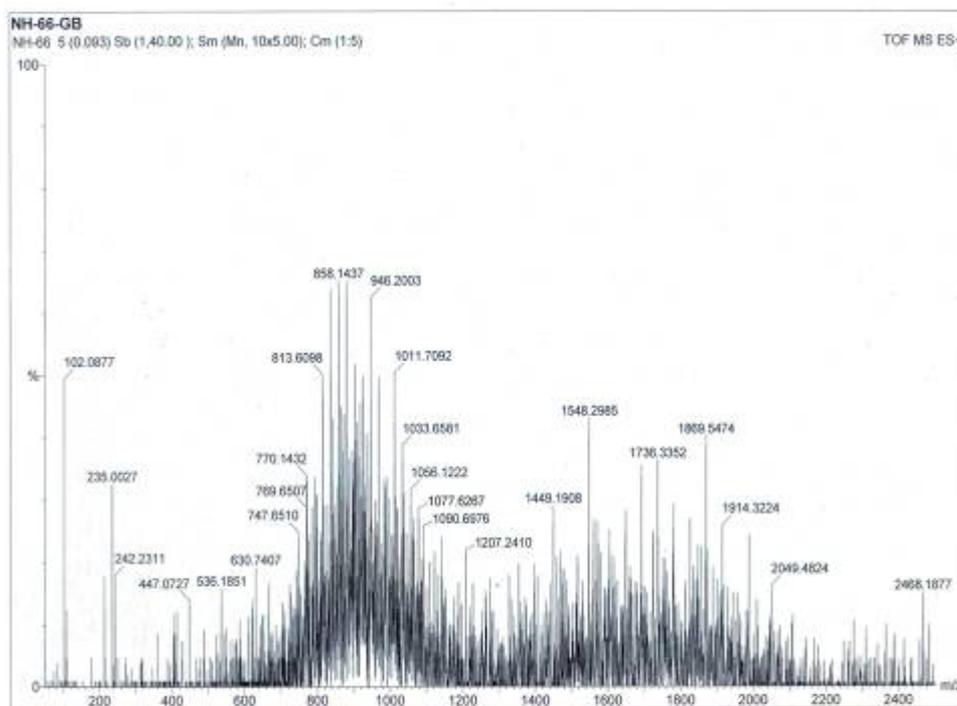


Fig 1. Mass spectrum of the polymeric sensor.

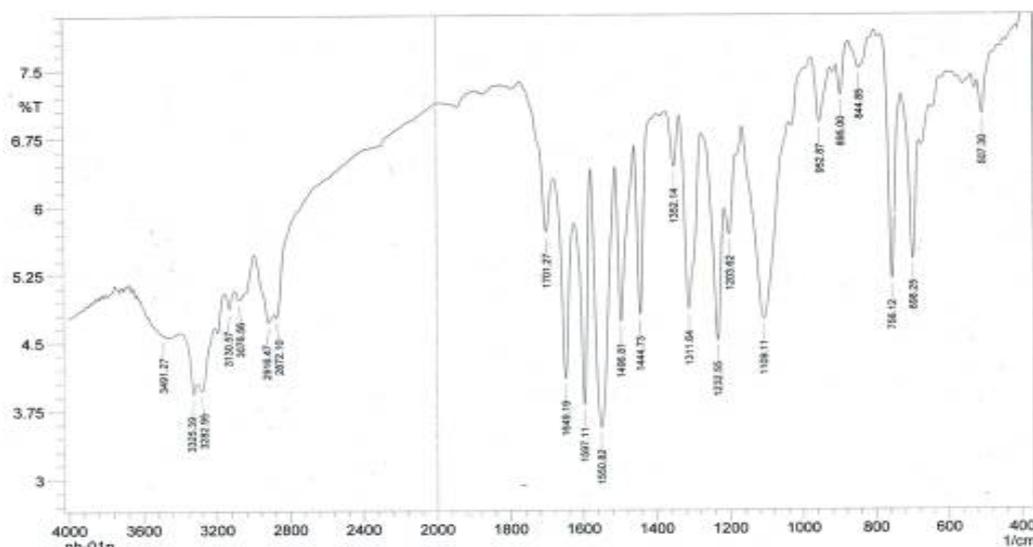


Fig.2 IR Spectrum of the polymeric sensor.