



# Anion Binding Poly (*p*-Aryltriazole) with High Affinity to Fluorine

Okerio J<sup>1\*</sup> and Neliswa M<sup>2</sup>

<sup>1</sup>Department of Mathematics Chemistry & physics, University of Eastern Africa, Kenya

<sup>2</sup>Department of Chemistry, Nelson Mandela University, Kenya

**\*Corresponding author:** Jasper Okerio, Department of Mathematics Chemistry & physics, University of Eastern Africa, Baraton, PO Box 122-40500, Kenya, Tel: +254792003618; Email: jasperokerio@yahoo.com

## Research Article

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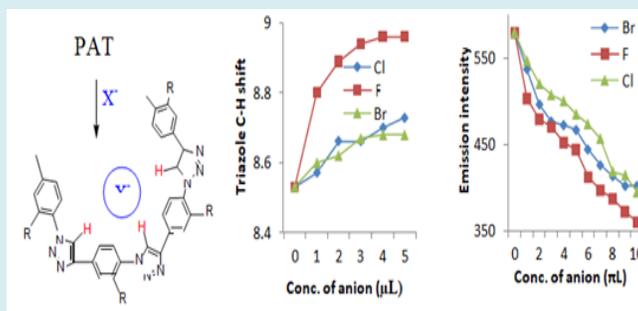
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## Abstract

Anion-binding polymer system based on click synthesized para (aryl-1,2,3-triazole) (PAT) functionality is described. The sensitivity and binding ability of the PAT system to halide ions such as F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> which involve re-organization of the aryl-triazole bonds, is explored using NMR and fluorescence spectroscopy. F<sup>-</sup> ion which induces the highest shift of the triazole C-H proton signal also shows the highest dynamic quenching of the PAT's fluorescent intensity compared to Br<sup>-</sup> and Cl<sup>-</sup> ions.



**Keywords:** Anion-binding Polymer; Polytriazoles; Phenyl-triazole; Halogen Ions

## Introduction

Recent studies have presented the triazole ring as multifaceted in functionality. Easily accessed via the Cu(I) catalyzed 1,3-dipolar cycloaddition (click) reaction of azides and acetylenes [1,2]. The triazole ring binds and forms complexes with cations, anions and neutral molecules. These properties are derived from the three electronegative sp<sup>2</sup> hybridized nitrogens which are nested on one side of the ring and the electropositive C-H group, which also offers minor steric hindrance [3-7]. Utilizing the C5-H, the triazole affords hydrogen bonds, with electronegative species, that are as strong as the classical, intrinsically polarized hydrogen bond donors (N-H and O-H) and plays an important role in the

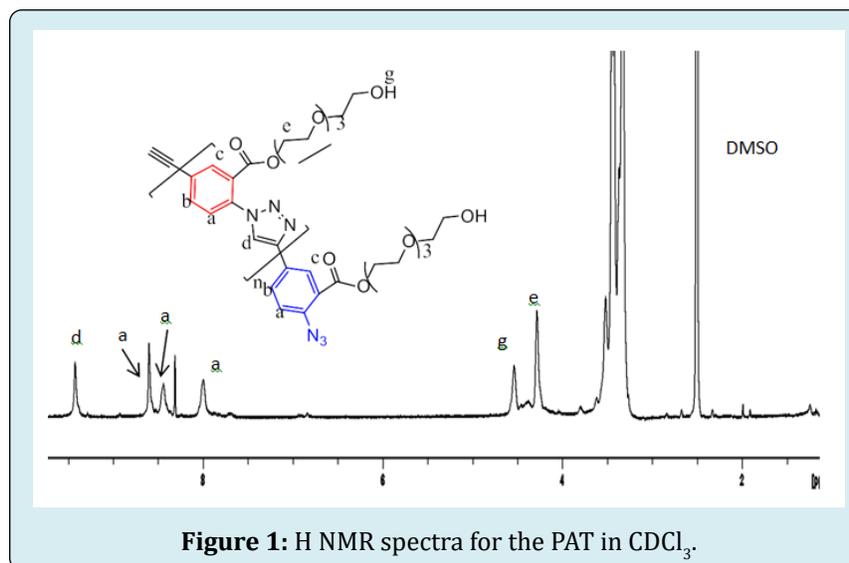
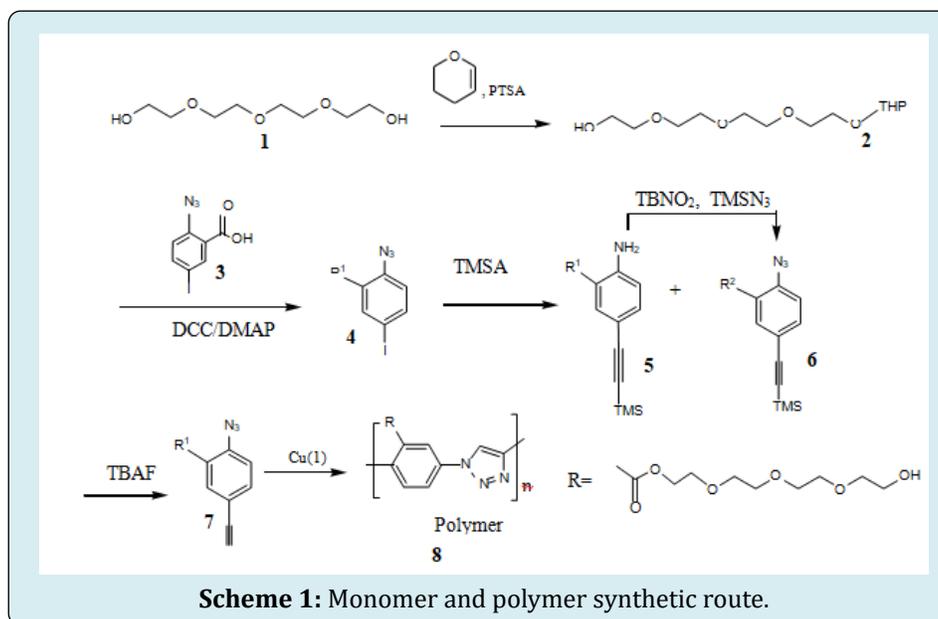
conformation, interaction, and recognition of both organic and inorganic structures [8]. Consequently, electron-deficient 1,4-diarylated 1,2,3-triazole derivatives form intermolecular bonds with halogens ions and other anions. Examples include a series of shape-persistent pre-organized triazolophanes, designed by Li and Flood [9], that binds the chloride ion with a high affinity and selectivity over all halide ions. A pre-organized triazole-based anion receptor with two hydroxyl groups on the central phenylene ring has been reported by Lee S, et al. [10]. Also, anion-binding light-induced triazole-based foldamer containing a photoresponsive azo-benzene in between the two phenyl-triazole oligomer units has been reported by Jiang, et al. [11].

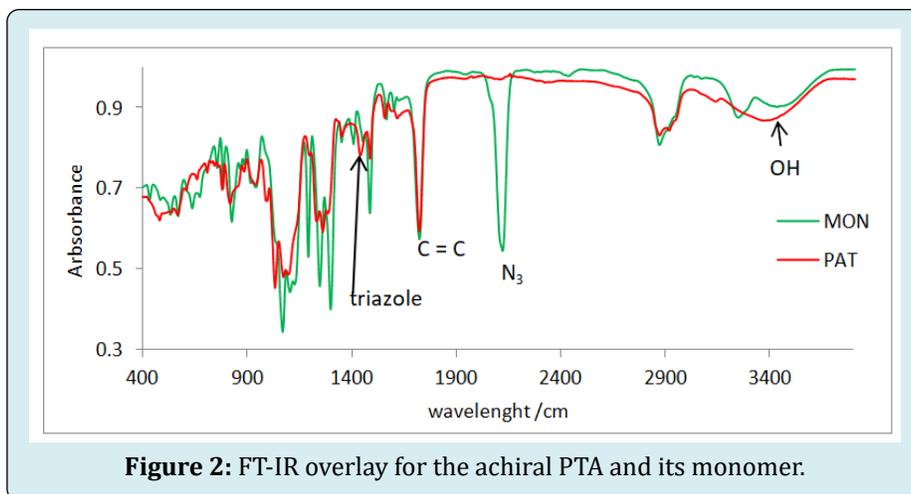
Herein, we show the electropositive triazole C-H atom of 1,2,3-triazole as a potent intramolecular hydrogen bond donor and the re-organisation or tuning of the conformation and/or shape of poly(*p*-aryl triazole)s backbone, synthesized via AB step growth click polymerization, following the hydrogen bonding pattern. Different anions are introduced to the polytriazoles and the changes in NMR and fluorescent properties arising from the binding effect of triazole moiety to the halogen ions are investigated.

### Experimental: Synthesis of Polymer

To afford polymers via the CuAAC reaction, terminal acetylene and azido functionalized aryl monomer was required. However, the anticipated polymer would have aromatic repeating units in the backbone that are known to

exhibit poor due to  $\pi$ - $\pi$  stacking and the aromatic backbone rigidity. With this in mind, tetraethylene glycol substituents were incorporated in the structure of the monomer to improve solubility of the resultant, otherwise insoluble aryltriazole polymers. Acid-catalyzed THP hydroxyl protection afforded mono-protected tetraethyl ethylene glycol **2**. The aryl group **3** was then coupled to alcohol **2** under DMAP/DCC catalysis followed by Palladium catalysed cross-coupling of aryl iodide with TMS-acetylene and acid catalysed THP deprotection of the alcohol, respectively, affording the TMS-protected aryl alcohol **6**. Finally, TBAF-catalysed desilylation afforded the required monomer **7**. The poly(*p*-aryl triazole) **8** was synthesized in high yields and considerable molecular weight, via CuAAC [1,2] from *p*-terminal alkyne functionalized ary-azide monomer shown (Scheme 1).



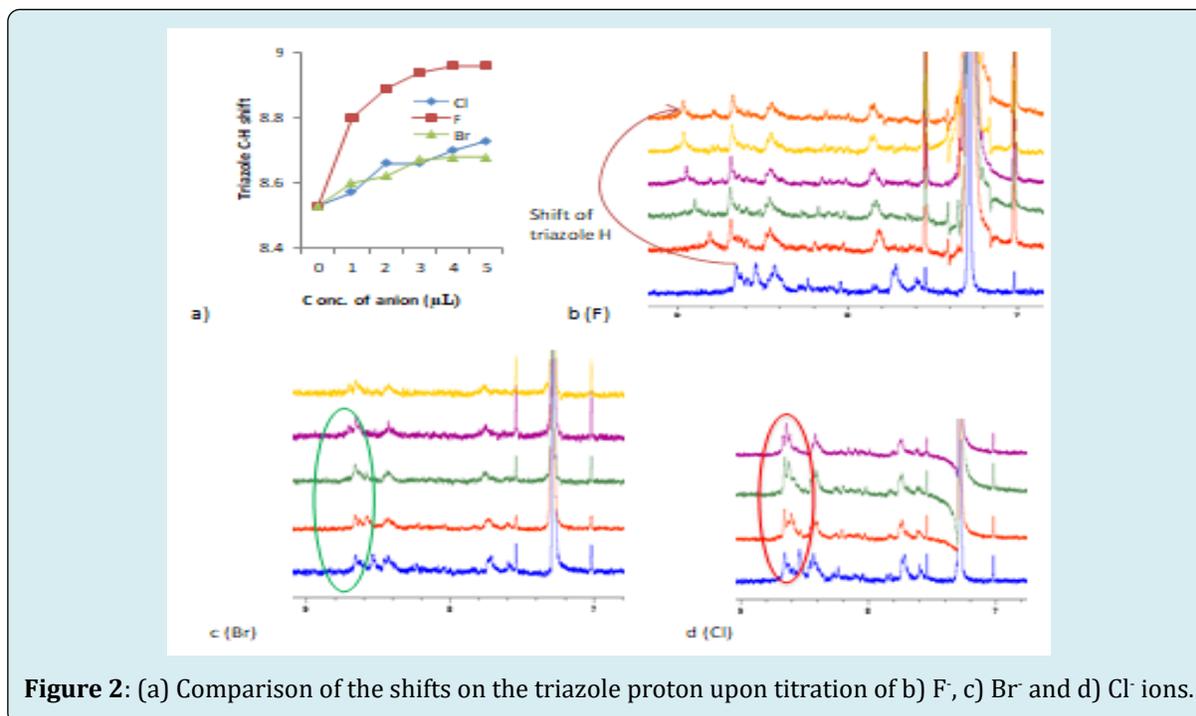


The structure of the PAT was confirmed by  $^1\text{H}$  NMR (Figure 1) and FTIR spectra (Figure 2). Besides the up-shifting of the polymeric proton signals compared to the monomer, the characteristic triazole ring C-H signal is observed at 8.53 ppm while the monomeric alkyne proton signal at 3.11 ppm disappears.

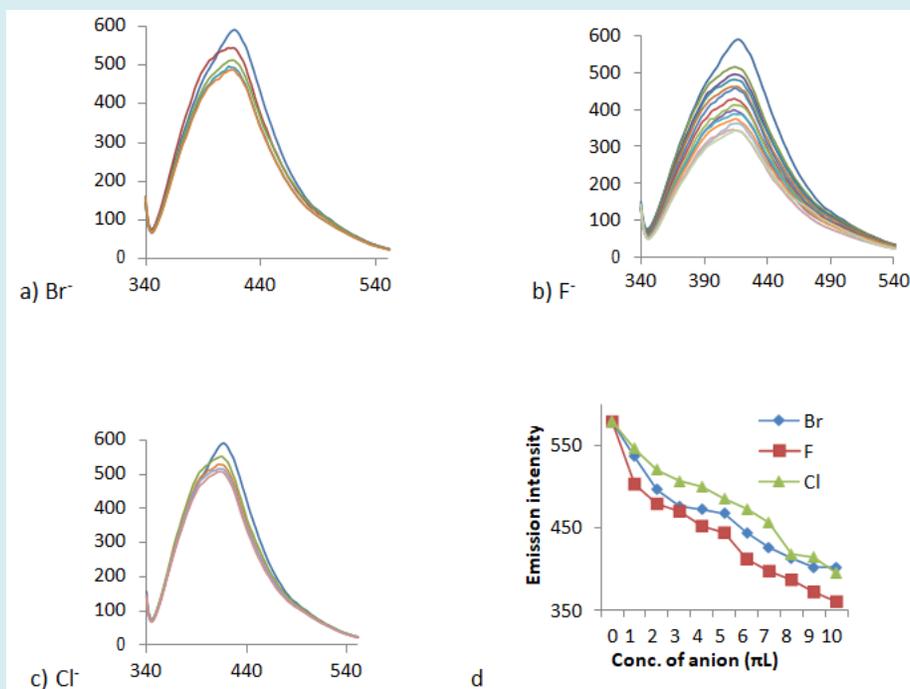
## Results and Discussion

Considering the triazole ring as a functional group that can coordinate and form complexes with anions as shown in the (Scheme 2), we set out investigate the ability of the PAT to bind and form complexes with halide ions through the changes in the PAT's NMR and fluorescence spectra upon

introduction of  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  ions using their tetra butyl ammonium sources. Titration of these anions into the PCT solution in  $\text{CDCl}_3$  induced significant shifts of the triazole C-H proton signal in the  $^1\text{H}$  NMR spectra.  $\text{F}^-$  ion induced the highest shift of the triazole C-H proton signal from 8.53 ppm for the uncoordinated PAT to 8.96 ppm upon titration of up to 6  $\mu\text{L}$  as shown in the partial proton NMR (Figure 2). This shift of triazole C-H proton signal confirms the participation of triazole C-5 proton, as hydrogen bond donor, in the coordinating the halide anion. The same trend is observed upon titration of  $\text{Cl}^-$  and  $\text{Br}^-$  ions but with weaker shifts from 8.53 ppm for the uncoordinated PAT to 8.73 ppm and 8.68 ppm upon titration of up to 6  $\mu\text{L}$ , respectively as shown in Figure 2.



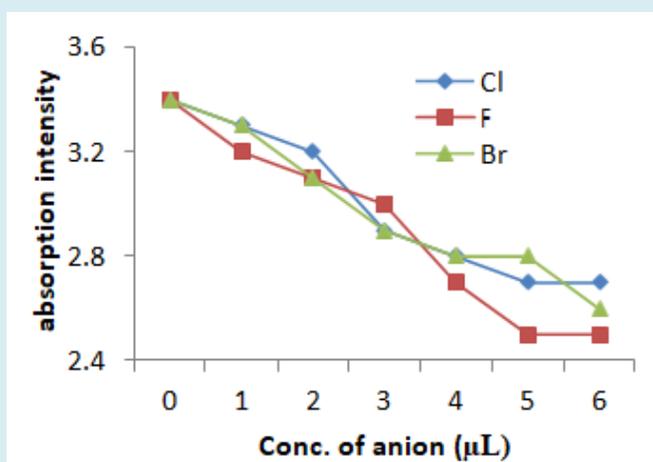




**Figure 5:** (a) PAT emission quenching upon titration of a) Br<sup>-</sup>, c) F<sup>-</sup>, d) Cl<sup>-</sup> ions and d) Job plot for the PAT emission quenching by Br<sup>-</sup>, F<sup>-</sup>, and Cl<sup>-</sup> ions.

The quenching is attributable to the electron transfer resulting from the collisions between the PAT and the quenchers. In comparison to Br<sup>-</sup> and Cl<sup>-</sup>, the pronounced quenching upon introduction of F<sup>-</sup> can be attributed to higher electron affinity arising from its high nuclear charge.

The same results were observed with absorption intensity as shown in Figure 3. The PAT displays more pronounced UV Vis quenching effect from F<sup>-</sup> compared to Br<sup>-</sup> and Cl<sup>-</sup> upon titration of the ions into PAT 8 solution in chloroform.



**Figure 6:** Job plot for PAT 8 UV Vis quenching upon titration of Cl<sup>-</sup>, F<sup>-</sup>, and Br<sup>-</sup> ions.

## Conclusion

In conclusion, a PAT has been prepared in good yields from azide and alkyne functionalized monomer, demonstrating the facile modularity click chemistry. Halide recognition by

the PAT was observed with higher affinity to F<sup>-</sup> ion with the PAT in chloroform. This PAT, therefore, will be well-suited for basic studies of triazole as donor for hydrogen, with the present study clearly showing the importance of aromatic CH H-bond donors in binding anions.

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