Synopsis

The content of this synopsis report entitled **"Newly Developed Conjugated Polymer Systems for Nitroexplosive Detection: Insights into the Mechanistic Investigations"** is divided into six chapters. Chapter 1 specifically describes the respective research area where the scope and significance of the subsequent chapters are discussed. Chapter 2 discusses about the synthesis and characterization of conjugated polymer (PFAM) and its application in the rapid and specific recognition of nitroexplosive-picric acid (PA) on solid support and in solution based on IFE/PET mechanism. Chapter 3 describes the synthesis of a new water-soluble non-fluorescent cationic conjugated polyelectrolyte PPPy, which selectively recognized nitroexplosive PA by fluorescence "turn-on" in the presence of closely related nitroexplosive compounds via fluorescence indicator displacement assay (IDA) technique in water at pH 7.0. Chapter 4 highlights the synthesis of cationic CP PFBT *via* oxidative polymerization and displayed dual state emission in DMSO as well as in water, a phenomenon very rarely observed, and tested for nitroexplosive analytes detection to observe a remarkable fluorescence quenching response for picric acid (PA) in the both solvents. Contact mode detection of PA was also accomplished using easy, economical and portable fluorescent test strips for on-site detection, which can detect upto 0.22 attogram level of PA. Vapor phase detection of PA was also established, which can detect up to 42.6 ppb level of PA vapors. Interestingly, the mechanism of sensing in DMSO solvent was attributed to strong inner filter effect (IFE) and photo induced electron transfer (PET), while in H_2O the sensing occurs via possible resonance energy transfer (RET) and photoinduced electron transfer (PET), which is exceptional and not reported earlier for a single probe. Chapter 5 discusses the synthesis of the neutral "receptor-free" highly fluorescent conjugated polymers (PF1 and PF2), which detects PA by a fluorescence turn-off response, and was found as a result of exclusive IFE and was further confirmed via IFE corrections. Chapter 6 summarizes the thesis overview and the importance of various sensing mechanisms that can probably exist for nitroexplosive detection but not limited to these chemical entities. Additionally, the design principle of probes that can result in efficient sensing of picric acid via these mechanisms was also studied and presented.

Chapter 1: Introduction

Conjugated polymers (CPs) are typically organic macromolecules consisting of a backbone chain with alternating single and multiple bonds. The research on conducting polymers began in 1970's, when films of polyacetylene were found to exhibit profound increase in electrical conductivity when exposed to halogen vapors. In the year 2000, three scientists Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa, founders of the conjugated conducting polymer chemistry, won the Noble prize in chemistry for their discovery. Recently CPs became an important class of materials, which have been used in various emerging area of research such as field-effect transistors (FETs), polymer solar cells, light-emitting electrochemical cells (LECs), flat panel displays using OLEDs and chemical and bio-sensors. These wide range of applications are due to their distinguished delocalised π-bonds throughout the polymeric backbone, which is the origin of their emissive as well as conductive property. CPs can be obtained with a variety of polymeric backbones like poly(para-phenylenes) (PPP), polypyrrole (PPy), polyfluorene (PF), poly(para-phenylene vinylene) (PPV), poly(para-phenylene ethynylene) (PPE) and polythiophene (PT) **(Figure 1).**

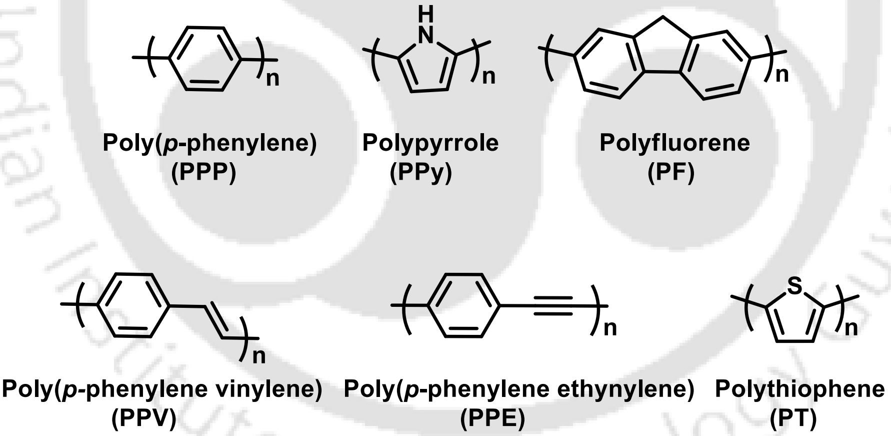

Figure 1. Structures of some well-known fluorescent conjugated polymer system.

Sensory signal amplification of CPs

CPs have more advantages than small molecular sensors because they are able to amplify the signal from a single binding event. The signal amplifying model of CPs was proposed by Swager group in 1995 and termed it as "molecular-wire effect" (**figure 2**). The conceptual basis of the signal amplification of the fluorescence sensory signal generated by CP is based upon binding with a target analyte. When an analyte binds locally to a receptor on a CP repeat unit the entire conjugated backbone is affected due to its 1-

dimensional wire-like property and the fluorescence of the entire polymer chain is altered. This results in an amplification of fluorescence when compared to small molecule sensors because a binding event on a small molecule only causes a single chromophore to change its fluorescence, whereas a CP binding event affects the fluorescence of an entire chain of chromophores by energy migration through the conducting polymer backbone. This amplification of signals provided by CPs is important for sensing applications because the molecules being analysed are often present in extremely dilute concentrations.

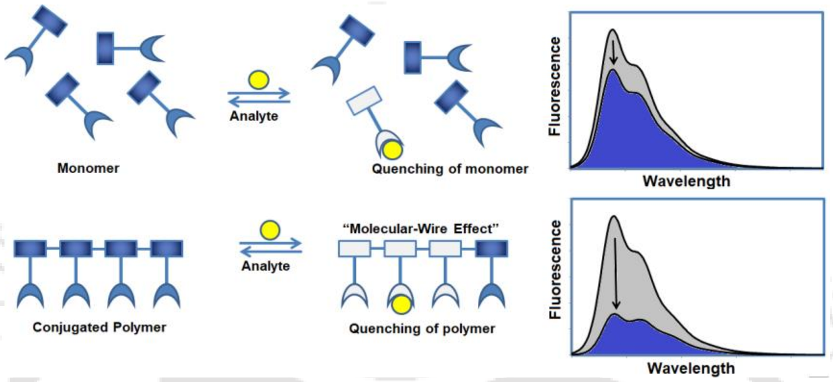

Figure 2. Pictorial representation of fluorescence quenching in monomer and polymer by analyte molecules.

Applications of conjugate polymeric systems in nitroexplosive sensing

CPs are one of the most promising class of materials for the recognition of nitroexplosives both in liquid phase as well as thin films owing to their high quantum efficiency, excellent molar absorptivity and high signal amplification via the "molecular wire effect". CPs provide unique optical properties and viability of distinguished receptor sites making them a desirable sensory candidate for detection of nitroexplosive at ultra-trace levels. Hence, in the recent year, researchers have designed various CPs and studied their potential application in detection of nitroexplosive-PA **(Figure 3)**, and explored distinguished mechanisms of sensing **(Figure 4)**.

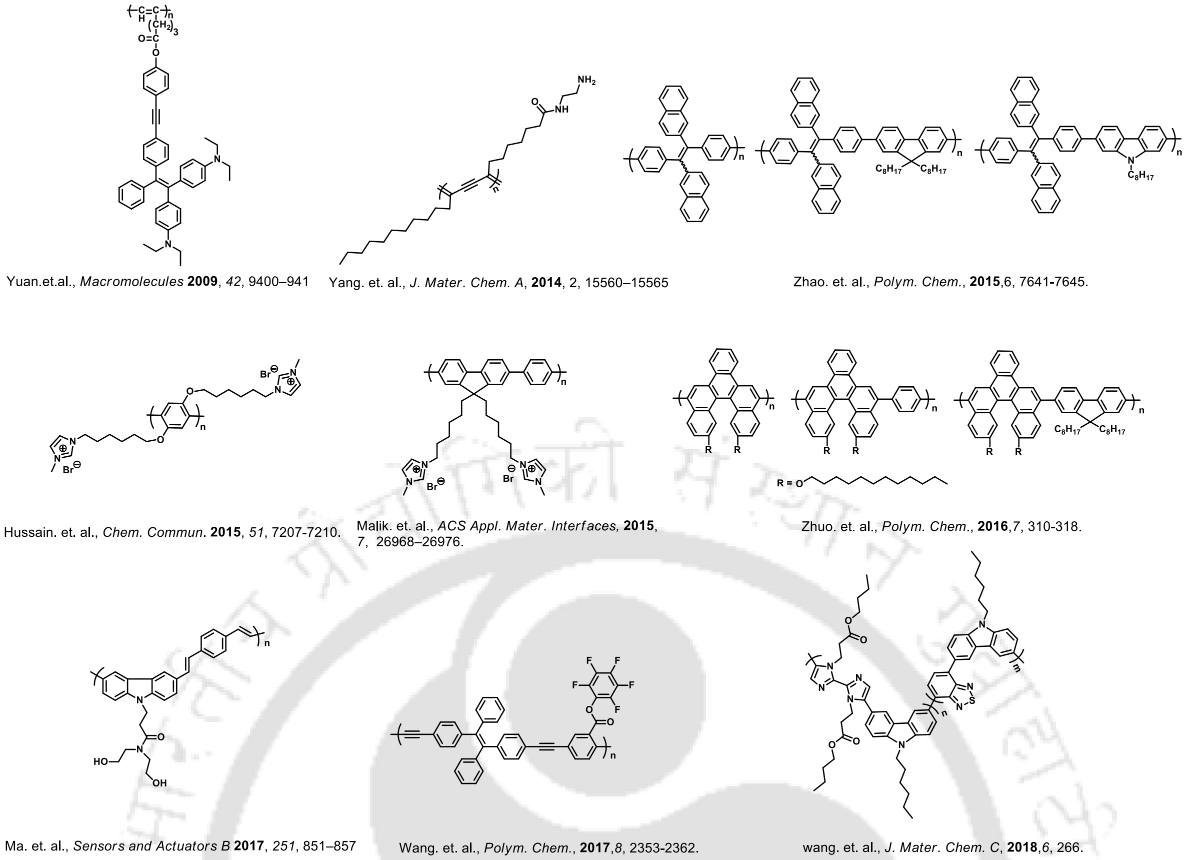

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Figure 3. Structures of some conjugated polymer system used for PA detection.

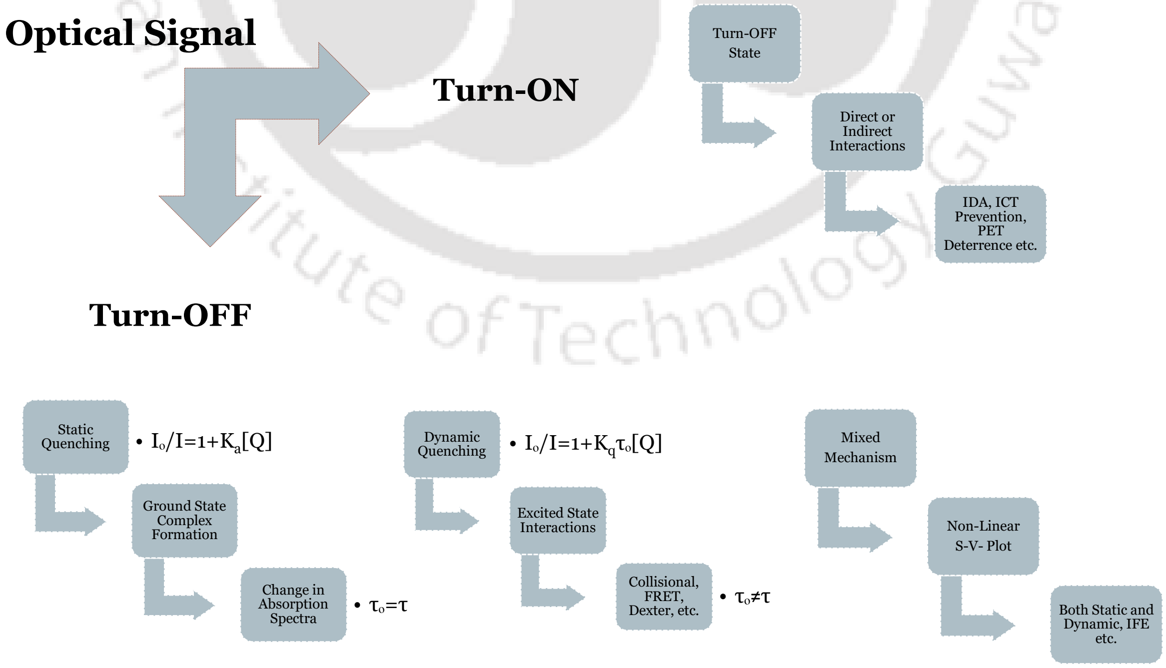
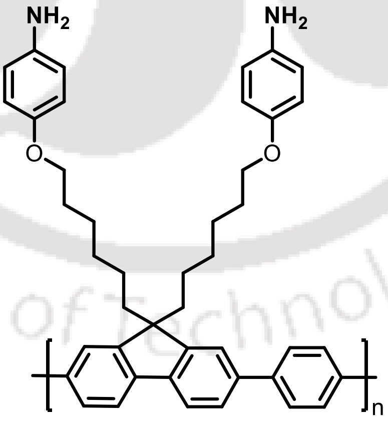


Figure 4. Flow chart representing various possible mechanism of sensing.

Chapter 2: Inner Filter Effect Based Selective Detection of Nitroexplosive-picric Acid in Aqueous Solution and Solid Support Using Conjugated Polymer

This chapter describes the synthesis of a new polyfluorene derivative, poly[4,4′-(((2-phenyl-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(oxy))-dianiline)] (PFAM) as shown in **Figure 5** *via* Suzuki coupling polymerization method in high yields for the rapid and specific recognition of nitroexplosive picric acid (PA) at 22.9 picogram level on solid support using paper strips and at 13.2 ppb level in aqueous solution. The polymer PFAM was well-characterized by means of NMR, UV−vis, fluorescence, time-resolved photoluminescence (TRPL) spectroscopy and cyclic voltammetry. The amplified signal response exclusively for PA was achieved via a strong inner filter effect (IFE), a phenomenon different from the widely reported ground-state charge transfer and/or Förster resonance energy transfer (FRET) based probes for nitroaromatics detection. Pendant amine groups attached on the side chains of PFAM provide enhanced sensitivity and exceptional selectivity via protonation assisted photoinduced electron transfer (PET) even in the presence of most common interfering nitroexplosives, as well as other analytes usually found in natural water. Thus, the PFAM based platform was demonstrated for monitoring traces of PA at very low levels even in competitive environment in solution as well as solid state **(Figure 6).**



(PFAM)

Figure 5. Structure of poly[4,4′-(((2-phenyl-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(oxy))-dianiline)] (PFAM).

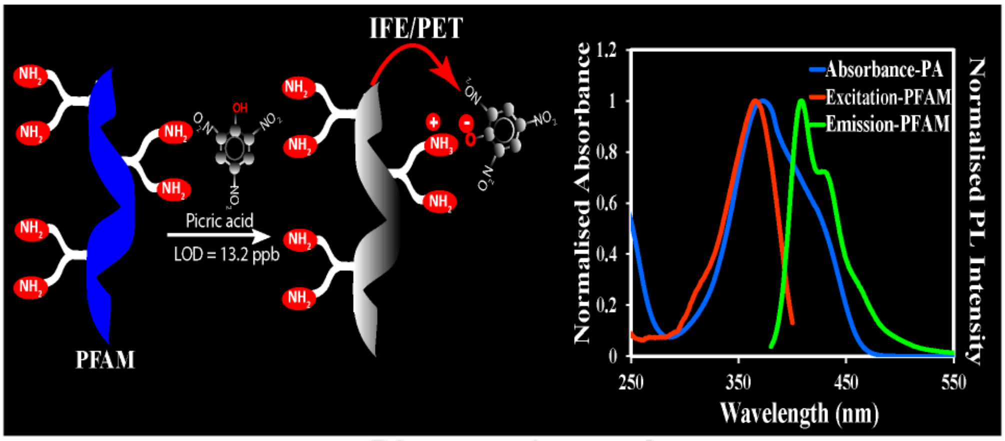
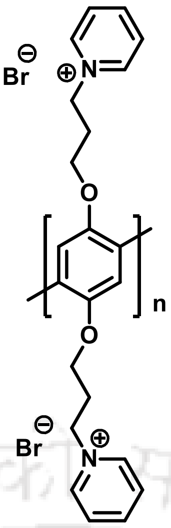


Figure 6. Schematic representation for the detection of picric acid by PFAM.

Chapter 3: Fluorescence "Turn-On" Indicator Displacement Assay Based Selective Detection of Nitroexplosive-picric Acid in Aqueous Media via a Cationic Conjugated Polyelectrolyte and Dye Complex

This chapter discusses about the synthesis of a new water-soluble nonfluorescent cationic conjugated polyelectrolyte poly(1,1′-((1,4-phenylenebis(oxy))bis-(propane-3,1-diyl))bis (pyridin-1-ium)bromide) (PPPy) (**Figure 7**) via an economical method of oxidative coupling polymerization in high yields. PPPy selectively recognized nitroexplosive picric acid (PA) by fluorescence "turn-on" in the presence of closely related nitroexplosive compounds, namely, 2,4,6-trinitrotoluene, 2,4-dinitrophenol, and 4-nitrophenol via fluorescence indicator displacement assay (IDA) technique in water at pH 7.0. The polymer PPPy was characterized by NMR spectroscopy, gel permeable chromatography, UV−vis spectroscopy. The polymer PPPy forms an electrostatic complex with uranine dye. This ensemble scheme was utilized to detect PA with a limit of detection (LOD) value of 295 nM (solution state) and 0.22 ppm (vapor state) through IDA, a phenomenon that is very different from the widely reported Förster resonance energy transfer, photoinduced electron transfer, ground-state charge transfer and inner filter effect based probes used for nitroexplosive PA detection (**Figure 8**).



(PPPy)

Figure 7. Structure of poly(1,1′-((1,4-phenylenebis(oxy))bis- (propane-3,1-diyl))bis(pyridin-1-ium)bromide) (PPPy)

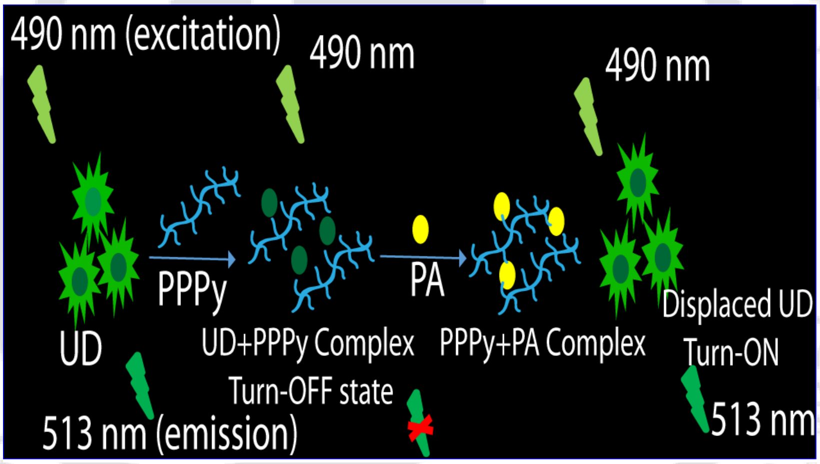
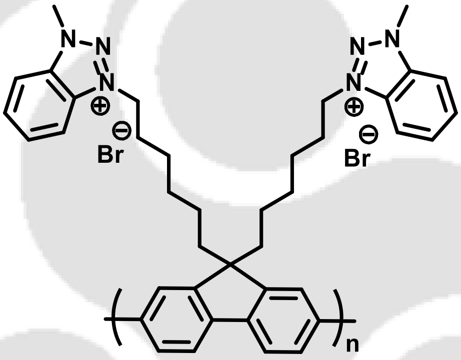


Figure 8. Schematic representation for the detection PA by IDA.

Chapter 4: Inner Filter Effect and Resonance Energy Transfer Based Attogram Level Detection of Nitroexplosive-Picric acid Using Dual Emitting Cationic conjugated Polyfluorene

In this chapter we have described the synthesis of a new a new cationic conjugated polyfluorene derivative, poly(3,3'-((9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(1-methyl-1H-benzo[d][1,2,3]triazol-3-ium) bromide) (PFBT) (**Figure 9**) using a simple and inexpensive method of oxidative coupling polymerization. The polymer PFBT displayed dual state emission in DMSO as well as in water, a phenomenon very rarely observed, and tested for nitroexplosive analytes detection to observe a remarkable fluorescence quenching response for picric acid (PA) in both solvents. The polymer PFBT was found to be highly sensitive and selective towards nitroexplosive PA in both the solvents (DMSO and H_2O) with exceptional quenching constant values of 2.69 × 10^4 M^{-1} and 2.18 × 10^5 M^{-1} and a very low detection limit of 92.7 nM (21.23 ppb) and 0.19 nM (43.53 ppt) in respective solvents. Furthermore, contact mode detection of PA was also accomplished using easy, economical and portable fluorescent test strips for on-site detection, which can detect upto 0.22 attogram level of PA. Vapor phase detection of PA was also established, which can detect up to 42.6 ppb level of PA vapors. Interestingly, the mechanism of sensing in DMSO solvent was attributed to strong inner filter effect (IFE) and photo induced electron transfer (PET), while in H_2O the sensing occurs via possible resonance energy transfer (RET) and photoinduced electron transfer (PET), which is exceptional and not reported earlier for a single probe (**Figure 10**).



(PFBT)

Figure 9. Structure of poly(3,3'-((9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(1-methyl-1H-benzo[d][1,2,3]triazol-3-ium) bromide) (PFBT).

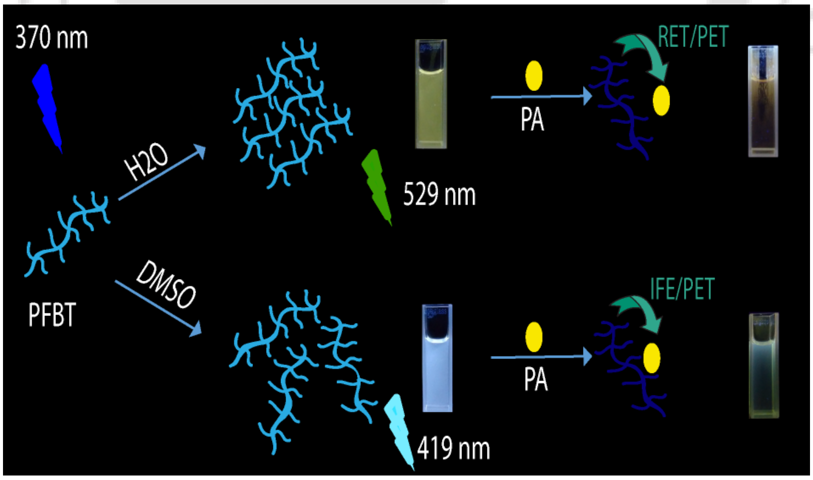
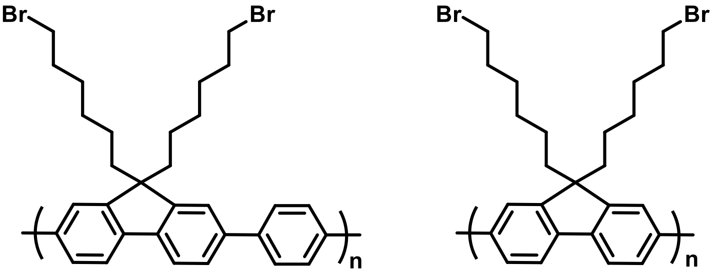


Figure 10. Schematic representation for the detection PA by PFBT.

Chapter 5: “Receptor Free” Inner Filter Effect Based Detection of Nitroexplosive-Picric Acid using two Polyfluorenes derivatives in solution and solid state and IFE corrections.

Previously inner filter effect (IFE) has been considered as an error in photoluminescence spectroscopy. Recently IFE has gained significance as one of the key cause of sensing mechanism in the area of chemical and biological sensing. IFE based sensing platforms provides simple and flexible sensing without any kind of interaction in between fluorophore and receptor. Therefore, it is quite challenging to design IFE based fluorophore and quencher combination. In this chapter, two “Receptor-free” fluorescent conjugated polymers of fluorene namely 9,9-bis(6-bromohexyl)-2-phenyl-9H-fluorene (PF1) and 9,9-bis(6-bromohexyl)-9H-fluorene (PF2) (**Figure 11**) were synthesized with slight modification in the main fluorescent backbone using Suzuki cross coupling polymerization and oxidative coupling polymerization methods with high yields respectively. The polymers were well characterized by gel permeable chromatography, NMR, UV-vis, fluorescence and time-resolved photoluminescence (TRPL) spectroscopies. The fluorescent polymers PF1 and PF2 explicitly recognize nitroexplosive picric acid (PA) among other nitroexplosive compounds used and displayed fluorescence quenching response in solution as well as on solid support via an IFE mechanism. The polymer, PF1 and PF2, were both found to be highly selective and sensitive towards the nitroexplosive PA with a high quenching constant value (K_{sv}) 5.1 × 10^4 M^{-1} and 5.0 × 10^4 M^{-1}, respectively and remarkably low LOD of 110 nM and 219 nM respectively. Contact mode detection of nitroexplosive PA was also performed using economical and transportable fluorescent paper test strips for on-site sensing, which can detect a minimum of 229.1 picogram level of PA. Earlier IFE mechanism for PA sensing has not been much explored in detailed and therefore we have studied it in detail and performed IFE correction for nitroexplosive PA and found ~ 77% suppression efficiency due to IFE (**Figure 12**).



(PF1) (PF2)

Figure 11. Structure of 9,9-bis(6-bromohexyl)-2-phenyl-9H-fluorene (PF1) and 9,9-bis(6-bromohexyl)-9H-fluorene (PF2)).

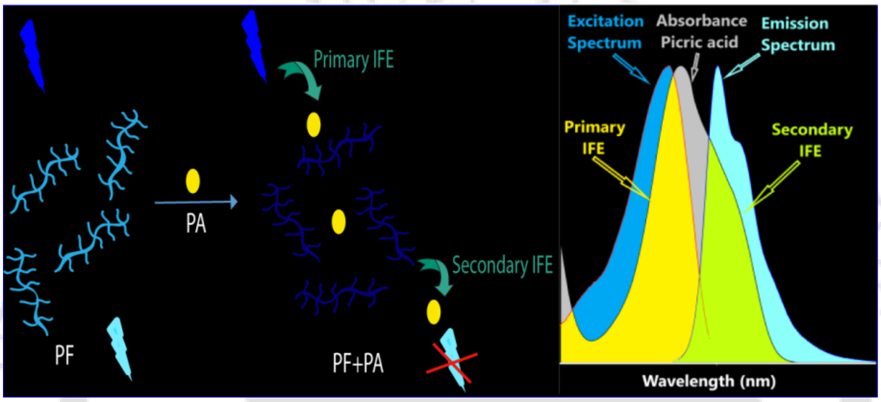


Figure 12. Schematic representation for the detection of PA by IFE mechanism.

Chapter 6

Thesis overview and Future Perspective

In summary, different types of conjugated polymeric systems have been designed, synthesized and utilized them in attaining simple, low cost and portable optical sensors capable of monitoring nitroexplosive-Picric acid (PA) at ultra-trace level. The mechanism of sensing for each of the CPs was studied in detail and explored. The conjugated polymer PFAM showed rapid and specific recognition toward PA on solid support and in solution based on IFE/PET mechanism. The non-fluorescent cationic conjugated polymer PPPy participates in indicator displacement assay resulting turn-on fluorescence selectively in presence of PA. The cationic conjugated polymer PFBT displayed substantial fluorescence quenching for PA in solution as well as solid state based on IFE and RET mechanism at attogram level of PA and utilised in making economical paper strips for on-site detection of nitroexplosive. The neutral “receptor-free” highly fluorescent conjugated polymers (PF1 and PF2) detect PA by a fluorescence turn-off response which was found as a result of exclusive IFE and was further confirmed via IFE corrections. All the CPs systems were found to be highly sensitive and selective towards nitroexplosive-PA.

Additionally, this thesis includes chemo-sensors based on fluorescence turn-off, indicator displacement assay and “receptor-free” sensing. To date, there are only countable reports available for the PA detection based on CPs. There is still scope for designing and exploring new sensing mechanisms, in order to achieve an ideal sensory system for nitroexplosive detection.