**Design, Synthesis and Characterization of Conjugated Polymers
for the Detection of Nitroaromatic Explosives and Isocyanates**

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ABSTRACT

The overall objectives of this thesis are (i) to synthesize and characterize a fluorescent polymer having the rigid pentyptycene and bulky cholesteryl ester groups, (ii) to characterize and compare the sensing properties of fluorescent polymers using standard lab fluorimeter and optic-fiber probe, and (iii) to study the effect of film thickness and compositions on the sensing properties.

A new conjugated polymer (**P1**) containing both the rigid pentyptycene and bulky cholesteryl ester groups was designed and successfully synthesized using the Sonogashira cross-coupling reaction. The monomers and the polymer were fully characterized by NMR and IR spectroscopy. Polymer **P1** had the weight-average molecular weight of 100,000 relative to polystyrene standard, inherent viscosity of 0.92 dL/g at 30 °C and the onset temperature of 288 °C for 5 % weight loss in nitrogen. The thin film of **P1** emits blue color with the maximum wavelength at 479 nm and the quantum yield of 0.30.

The fluorescence quenching properties of polymer **P1** thin films in response to vapor of 2,4-dinitrotulene (DNT) have been investigated by varying the film thickness, applying a undercoating of (3-aminopropyl)triethoxysilane (APTES) and blending with another polar polymer. A significant change in fluorescence intensity (51 % in 60-s) in response to DNT vapor exposure at ambient temperature was achieved when the polymer film coated on glass plate was about 2 nm in thickness. In comparison with the film of polymer alone, the film undercoated with 5-20 nm thick APTES and the film of polymer blend showed additional 18.5 % (in 20-s exposure) and 18.7 % (in 5-min exposure) decrease in fluorescence intensity, respectively. The use of polymer or polymer blend coated on optic-fiber tip for detection of DNT vapor has also been demonstrated. In

comparison, an analogue polymer (**P2**) shows a larger fluorescence quenching percentage and faster response for a given time.

Polymers **P1** and **P2** showed rapid fluorescence quenching response upon exposure to isocyanate vapor at ambient temperature, especially for aromatic isocyanates of industrial importance such as PPDI, TDI and NDI. Considering the synthesis and sensing performance, polymer **P2** is the better candidate for isocyanate sensing.

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TABLE OF CONTENTS

Abstract	ii
Acknowledgments	iv
List of Tables	viii
List of Figures	ix
List of Schemes	xi
List of Charts	xi
Chapter I.	Introduction
I.1.	Background and Motivation
I.2.	Explosives and Detection Methods
I.3.	Isocyanates and Current Detection Methods
I.4.	Fluorescent Polymers for Chemical Sensing
I.5.	Fluorescence Turn-Off Sensing Mechanism
I.6.	Fiber-Optic Sensing
I.7.	Design Rationale and Objective
	Reference
Chapter II.	Synthesis and Characterization of Monomers and Polymer

II.1. Overview of Sonogashira Cross-coupling Reaction	20
II.2. Synthesis of Polymer P1	23
II.3. Characterization of Monomers and Polymer P1	28
II.3.1. Characterization of Monomers	28
II.3.2. Characterization of Polymer P1	33
II.4. Fluorescence Property of Polymer P2	39
II.5. Conclusion	41
II.6. Experimental Section	42
II.6.1. Materials	42
II.6.2. General Characterizations	42
II.6.3. Film Preparation	43
II.6.4. Syntheses	44
References	49
 Chapter III. DNT Vapor Detection	
III.1. Preparation of Polymer Films	52
III.2. Detection of DNT Using Films Coated on Glass Plate	53
III.3. Effect of Film Thickness	54

III.4. Effect of Undercoating	57
III.5. Effect of Polymer Blending	59
III.6. Fiber-Optic Sensing	60
III.7. Comparison of Polymers P1 and P2	63
III.8. Conclusion	63
III.9. Experimental Section	64
References	65
Chapter IV. Isocyanate Vapor Detection	
IV.1. Target Isocyanates and Their Properties	67
IV.2. Selection of Sensory Polymers for Isocyanate Detection	70
IV.3. Detection of Isocyanates Using Polymer P1	71
IV.4. Detection of Isocyanates Using Polymer P2	75
IV.5. Conclusion	78
IV.6. Experimental Section	79
References	80
Appendix A. ^1H and ^{13}C NMR Spectra and Assignments of Compounds 3-6	83
Appendix B. ^1H and ^{13}C NMR Spectra and Assignments of Compound 9	87

LIST OF TABLES

I.1.	Vapor pressure of some explosive compounds	4
II.1.	^1H and ^{13}C NMR assignments of monomers 7 and 11	30
II.2.	^1H and ^{13}C NMR assignments of polymer P1	34
II.3.	Photophysical property of polymer P1	38
III.1.	Increase in fluorescence quenching response of P1 films on glass plate with and without APTES undercoating	59
III.2.	Increase in fluorescence quenching response of polymer blend films relative to P1 films on glass plate	60
IV.1.	Vapor pressures and vapor concentrations of target isocyanates	69
IV.2.	FQR of P1 film (25-30 nm thickness) to isocyanates at 5 minutes	72
IV.3.	FQR of P1 film (2-3 nm) to vapors of PPDI, TDI and NDI at given times	75
IV.4.	FQR to isocyanates (P2 film in 2-3 nm thickness) at 5 minutes	77
IV.5.	FQR of films (2-3 nm) of P2 to vapors of PPDI, TDI and NDI at given times	78

LIST OF FIGURES

I.1.	Structures of some explosives	3
I.2.	Demonstration of amplified quenching in a CP	7
I.3.	Structures of PPEs	9
I.4.	Electron-transfer fluorescent quenching mechanism	10
I.5.	Fluorescent polymers containing cholesteryl ester groups	13
I.6.	Structure of polymer P2	14
II.1.	^1H NMR (300 MHz, CDCl_3) spectrum of monomer 7	31
II.2.	^1H NMR (300 MHz, CDCl_3) spectrum of monomer 11	31
II.3.	^{13}C NMR (75 MHz, CDCl_3) spectra of monomer 11	32
II.4.	The absorption and fluorescence spectra of monomers 7 (dashed lines) and 11 (solid lines) in chloroform solutions	33
II.5.	^1H NMR (300 MHz, CDCl_3) spectrum of P1	35
II.6.	^{13}C NMR (75 MHz, CDCl_3) spectrum of P1	36
II.7.	Absorption and fluorescence spectra of P1 in chloroform (solid lines) and in spin-coated films (dashed lines)	39
II.8.	Fluorescence spectra of P1 film coated on glass plate (solid line) and on optic-fiber (dash-dotted line)	39
II.9.	Absorption (dotted line) and emission (solid line) spectra of P2 film (excited at 350 nm)	41
III.1.	The time-dependent PL spectra (excitation at 390 nm) of P1 (spin-coated film 10 nm) upon exposure to DNT vapor at room temperature at 0, 30, 60, 120, 180 and 300s. Inset: Fluorescence quenching response over time	54
III.2.	Fluorescence quenching response of films of P1 in different thickness after 10-60 seconds of exposure to DNT vapor	56
III.3.	Fluorescence quenching response of films of P1 in different thickness after 1-5 min of exposure to DNT vapor	56

III.4.	Schematic drawing of an experimental setup for fiber-optic sensing	61
III.5.	Fluorescence quenching response of P1 film (ca. 30 nm thickness) coated on optic-fiber tip	62
IV.1.	Some isocyanate reactions	68
IV.2.	Structures of target isocyanates	69
IV.3.	Structures of polymers P1 and P2	70
IV.4.	The time-dependent PL spectra (excitation at 390 nm) of P1 (2-3 nm thickness) upon exposure to TDI vapor at room temperature at the time of 0-600s	71
IV.5.	Fluorescence quenching response of P1 film (2-3 nm) to TDI vapor during 0-10 minutes	72
IV.6.	FQR to vapors of PPDI, TDI and NDI at 60-s exposure, using P1 films in 2 nm and 25 nm thickness	74
IV.7.	The time-dependent fluorescence intensity of P2 film (2-3 nm) upon exposure to TDI vapor (room temperature) at 0, 10, 20, 30, 40, 50, 60, 90, 120, 180 and 240s (top to bottom). Inset: FRQ (%) as a function of time	76
IV.8.	The time-dependent fluorescence intensity of P2 film (2-3 nm) upon exposure to PPDI vapor (room temperature) at 0, 10, 20, 30, 40, 50, 60, 90 and 120s (top to bottom). Inset: FRQ (%) as a function of time	76
IV.9.	FQR to vapors of PPDI, TDI and NDI at 60-s exposure, each pair are done by 2 nm and 33 nm P2 films, respectively.	77

LIST OF SCHEMES

I.1.	Synthesis of conjugated polymer P1	14
II.1.	The Sonogashira cross-coupling reaction	20
II.2.	Sonogashira reaction mechanism	22
II.3.	Synthetic route to compound 4	23
II.4.	Synthetic route to compound 7	24
II.5.	Synthetic route to dibromo monomer 11	25
II.6.	Mechanism of acylation	27
II.7.	Mechanism of esterification	27
II.8.	Synthesis of polymer P1	28
II.9.	Synthetic route to polymer P2	40
III.1.	Illustration of film thickness effect on the fluorescence quenching displayed by nitroaromatics	57

LIST OF CHARTS

I.1.	Classification of explosives based on structure, performance and sensitivity	3
IV.1.	Order of relative sensitivity of isocyanates detected by polymer P1	73

CHAPTER I

Introduction

I.1 Background and Motivation

In recent years, the need for sensitive and selective detection of trace amounts of chemicals such as toxic industrial materials (e.g., isocyanates), hazardous air and automobile emission pollutants, radionuclides and wastes, biologically-active substances (such as endocrine-disrupting chemicals), and explosives has increased greatly¹. The primary concern is the effect of these chemicals on the quality of the water, air, soil and food, which may have damaging health effects. The public safety is another concern.

With the recent rise in global terrorist threats and general availability of high explosives, law enforcement agencies around the world are faced with the problem of detection explosive devices in luggage, courier packages, vehicles, and aircrafts². Explosive-based terrorism has become so popular, because explosive-based weapons are simple, easy to deploy, and can cause enormous damage³⁻⁵. Furthermore, the explosive compounds can release from their initial deployment sites into the environment and cause harmful effects to all life forms. They can rapidly penetrate the skin and cause the formation of methemo-globin on acute exposure and anemia on chronic exposure. A common explosive is 2,4,6-trinitrotoluene (TNT), which can readily enter groundwater supplies and make the water toxic at above 2 ng.ml⁻¹ and cause liver damage and aplastic anemia⁶. Therefore, the detection of explosive materials is highly required for preventing terrorist activities and damaging effects on the health of the population.

I.2 Explosives and Detection Methods

Trace detection of explosives typically involves collecting vapor or particulate samples and analyzing them with a sensor system. Currently, among many different

techniques known for detecting trace explosives, metal detectors and ion mobility spectrometry are commonly used, but must be calibrated frequently⁷⁻⁹. Other methods such as surface enhanced Raman spectroscopy, mass spectrometry and energy dispersive X-ray diffraction are highly sensitive but are either expensive or require time-consuming procedures¹⁰⁻¹⁴. A simple, inexpensive alternative to these methods are chemical sensors: molecular devices that are designed to detect a specific class of explosive molecules, such as TNT^{5,15}.

In order to detect explosives using chemical sensors, it is important to understand their physical and chemical properties. Explosives contain chemical compounds that can be initiated to undergo self-propagating decomposition resulting in the sudden release of heat and pressure. There are high and low explosives based on their burn rates (Chart I.1). High explosives are further divided into primary and secondary explosives based on their stability. Primary explosives, such as lead azide, are extremely sensitive to external stimuli such as friction and thermal or electrical sparks for initiating explosion. Secondary explosives, such as TNT and RDX, are relatively stable and require primary explosives to initiate the explosion. TNT has been studied much more than other explosives, because it is a main component in more than 10 types of bombs, especially those used in landmines¹⁵. DNT (2,4-dinitrotoluene) is an impurity component present in TNT explosives resulting from the preparation process¹⁶ (Figure I.1).

Chart I.1. Classification of explosives based on structure, performance and sensitivity
(Adopted from Ref. 20)

Figure I.1. Structures of some explosives

Most common explosives have extremely low vapor pressures at room temperature (Table I.1)¹⁷. The low vapor pressures indicate that these molecules are extremely sticky

and tend to adsorb to surfaces very easily. The explosive vapors can be collected by heating and condensing the sample rapidly on cold surfaces. However, the sticky nature of explosive molecules also causes condensation of the molecules during the diffusing into sensor systems. In addition, the vapor concentrations of explosives near a bomb may be 2–6 orders of magnitude less than their equilibrium vapor pressures after sealing in plastics^{18,19}. Therefore, trace sampling of these types of explosives with very low vapor pressures is a complicated issue. However, the presence of small amounts of DNT in TNT makes explosive detection possible due to the higher vapor pressure of DNT¹⁹.

Table I.1. Vapor pressure of some explosive compounds

Explosives	Molecular Weight	Vapor Pressure (torr) (at room temperature)
2,4,6-Trinitrotoluene (TNT)	227	1.1×10^{-6}
2,4-Dinitrotoluene (DNT)	182	1.5×10^{-4}
2,4,6-Trinitrobenzene (TNB)	213	2.2×10^{-4}
Pentaerythritol tetranitrate (PETN)	316	3.8×10^{-10}
Nitroglycerine (NG)	227	2.6×10^{-6}
Tetranitro-triazacyclohexane (RDX)	222	4.1×10^{-9}

I.3 Isocyanates and Current Detection Methods

Isocyanates are a family of highly reactive, low molecular weight chemicals with the functional group of --N=C=O . They are widely used in the manufacture of flexible and rigid foams, fibers, coatings such as paints and varnishes, and elastomers, and are increasingly used in the automobile industry, auto body repair, and building insulation⁴¹,

⁴². Spray-on polyurethane products containing isocyanates have been developed for a

wide range of retail, commercial, and industrial uses to protect cement, wood, fiberglass, steel and aluminum, including protective coatings for truck beds, trailers, boats, foundations, and decks²¹. The most widely used compounds are diisocyanates, which contain two isocyanate groups and are manufactured for reaction with polyols in the production of polyurethanes. The global market for diisocyanates⁴³ in 2000 was 4.4 million tons. The most commonly used diisocyanates include 4,4'-methylene diphenyl isocyanate (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI). Other important diisocyanates include naphthalene diisocyanate (NDI), p-phenylene diisocyanate (PPDI) and isophorone diisocyanate (IPDI)²¹.

Isocyanates are powerful irritants to the mucous membranes of the eyes and gastrointestinal and respiratory tracts²². Direct skin contact can also cause marked inflammation. Isocyanates can also sensitize workers, making them subject to severe asthma attacks upon continued exposure. Death from severe asthma in some sensitized subjects has been reported⁴⁰. Vapors of diisocyanates are corrosive and severely damaging to the eyes. Contact may cause permanent eye damage. Inhalation of fumes can cause various respiratory ailments. Isocyanates are widely used in industry and around 280,000 workers in the US⁴⁰ are potentially exposed; however, many workers are unaware of the potential hazards that these chemicals present in their work environment, which makes them more vulnerable. Preventing exposure to isocyanates is a critical step in eliminating their health hazard. Early recognition of sensitization and prompt and strict first aid measures are essential to reduce the risk of long-term or permanent respiratory problems for workers who have become sensitized. Currently, there are few respirators

available on the market with end-of-service life indicators; and there are few direct detectors that can sense the isocyanate vapor within 5 minutes.

Currently, the methods of detection of isocyanates are mainly instrument-based and require that the isocyanate be reacted with an amine. For example, hexamethylene diisocyanate can be recognized by GC with derivatization determination of 1,6-hexamethylenediamine; toluene isocyanate has been detected through reaction with toluenediamine in urine. The typical detection process contains three steps¹: sampling, instrumental determination (MS, GC and HPLC) and property tests (specific reaction and photophysical properties). Even though these methods are highly precise and sensitive, the instrument and equipment are too large, expensive and time-consuming or too sophisticated to handle and so these methods are not easily applied to in-the-field testing. The low vapor pressure of isocyanates, especially aromatic isocyanates, makes it difficult to collect and sample the vapors in air.

I.4 Fluorescent Polymers for Chemical Sensing

Fluorescence is widely used in chemical sensing. Aside from inherent sensitivity, this method offers diverse transduction schemes based upon changes in intensity, energy transfer, wavelength (excitation and emission), and lifetime^{30,31}. Fluorescent polymer chemical sensors are of particular interest due to their inherent sensitivity and simplicity. One of the most attractive features is that they do not require a separate reference sensor, as potentiometric chemical sensors do. Conjugated polymers (CPs) have found wide applications as fluorescent sensors, because of their high sensitivity to a variety of solution- and vapor-phase analytes²³⁻²⁹. The remarkable sensitivity of CP based sensor

devices as compared to small molecule sensors is attributed to the CPs' intrinsic ability to provide an amplified response to an analyte binding event. This amplification was first demonstrated by Zhou and Swager in 1995³⁴. Their studies confirm that the act of “wiring receptors in series” creates a higher sensitivity over a small molecule indicator³² (Figure I.2), as the conjugated polymer backbone can effectively transport electronic excited states (“excitons”). Excitons in CPs are very mobile and can diffuse throughout an isolated polymer chain or within polymer solids. Exciton migration increases the frequency of interaction with a bound quencher and results in the increased sensitivity^{32,33}.

Figure I.2. Demonstration of amplified quenching in a CP; the determination of the quenching reveals the constant for binding of paraquat to a single cyclophane receptor (top). In the polymer the larger (amplified) quenching constant reflects the fact that the quencher can be bound to any of the repeating units visited by the exciton (bottom)³⁸.

To demonstrate this principle, studies were conducted in parallel on a small molecule indicator containing a fluorescent monomeric cyclophane receptor, and polymeric analogues of different molecular weights. The cyclophane receptors were chosen to bind

paraquat which is a very effective electron-transfer quenching agent. The results show that both the monomer and polymer displayed quenching resulting from the binding of the paraquat by the cyclophane to form a rotaxane complex, but the polymer gives a greatly enhanced sensitivity over the monomeric compound. The origin of this effect comes from a facile energy migration along the polymer backbone to the occupied receptor sites (Figure I.2). In this scheme, the signal is amplified because the polymer need only have a small fraction of receptor sites occupied to affect complete quenching. In contrast with a monomeric indicator, every receptor must be occupied for complete quenching. Further investigations have also demonstrated that this effect is molecular weight dependent and at low to intermediate degrees of polymerization, the signal amplification increases with molecular weight. Once the molecular weight exceeds the average diffusion length of the excitation (ca. $M_n = 100000$), the effect is independent of molecular weight³⁴.

This sensing system has been successfully employed in land mine detection, since there are roughly 120 million unexploded land mines worldwide³⁵. Several kinds of CPs have been synthesized to detect aromatic explosives. Poly(p-phenyleneethynylene)s (PPEs) are one of the most successful products in this regard (Figure I.3). Further modification of the basic polymer structure by moving the electron-rich alkoxy group on the iptycene moiety improved the sensitivity and other sensing properties³⁶. PPE contain two bulky pentyptycene moieties on each alternating phenyl unit of the backbone, which hinder interchain π stacking and self-quenching of luminescence in the solid state. The long polymer chain allows exciton delocalization along the chain, which contributes to the outstanding sensitivity (Figure I.3). In polymer PPE-2, the electron-rich

dialkoxyphenyl rings on the iptycene can associate with the electron-deficient analytes via electrostatic and π - π interactions, which proves significantly the quenching ability compared to polymer PPE-1.

Figure I.3. Structures of PPEs

I.5 Fluorescence Turn-Off Sensing Mechanism

Most explosive compounds contain the nitro group (NO_2), and nitroaromatics explosives such as TNT are mainly employed in military applications or by terrorists. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty π^* orbital, thereby making these compounds good electron acceptors. As a result, reduction potentials become more favorable (less negative) as nitro substitution increases³⁷, compared to nitrobenzene (-1.15 V), DNT (-0.9 V), and TNT (-0.7 V). Excited state delocalization in fluorescent polymers is important because exciton migration increases the frequency of interaction with a bound quencher, which can contribute to enhanced detection sensitivity. Fluorescent, electron-rich conjugated

polymers have therefore been applied to the detection of nitroaromatic explosives in the vapor phase²⁵. The interaction between the conjugated polymer and the explosive analyte is often achieved through an electron donor-acceptor mechanism (also called charge transfer, CT), as depicted in Figure I.4. Electron deficient analytes, such as nitroaromatics, can act as electron acceptors for photo-excited electrons of the fluorescent polymers.

Figure I.4. Electron-transfer fluorescent quenching mechanism (Adopted from Ref. 18)

I.6 Fiber-Optic Sensing

Utilizing a thin film of fluorescent polymer in sensors has become the method of choice for explosive detection. There are several critical factors that could influence the efficiency of the fluorescent quenching method. A thicker film can generate a higher emission level due to the unquenched under-layer that does not interact with explosive compounds, and adversely affecting the quenching effect or sensing sensitivity. Thus, the

film thickness is crucial. However, nearly all the transparent thin films tend to absorb only a very limited amount of excitation light while giving a weak fluorescent signal.

Maximizing the efficiency of fluorescent light collection from the polymer film has become critical for ultra-trace sensing. Only for lower-energy illumination, the level of fluorescent signal is directly proportional to the level of excitation power. With high excitation energies, the polymer tends to degrade or is permanently damaged. Strong excitation can cause continuous drop in signal levels, which could produce a false quenching effect. These problems may arise from using conventional high-performance lab-based equipments such as a spectrophotometer or fluorimeter. Lab-based equipments are simple but not practical.

Fiber-optic sensing system may solve these problems. An optic-fiber probe coated with a thin film of sensory polymer can effectively collect the incoming fluorescent signal. The filtered signal light is then sent to a spectrometer and a computer system via a multimode fiber spectral display and analysis. The light source may be an argon laser or light-emitting diode. The fluorescent optic-fiber sensor can reduce stray of excitation light and signal fluctuation, enhance signal stability, and is up to 2.5 times more sensitive in a sensing capability over the conventional laboratory equipments. Optic fibers are low-cost, flexible and lightweight, with extremely low signal loss over long transmission distances. They can provide a portable and cost-effective explosive detection system and are capable of remotely accessing hard-to-reach areas.

I.7 Design Rationale and Objectives

Good electron acceptors can efficiently quench fluorescence by photoinduced electron transfer. Swager's pentiptycene-containing polymer is highly sensitive to TNT or DNT vapor and shows rapid quenching of its blue luminescence (465 nm) at sub-part-per-million (ppb) levels of analytes^{23,24}. Another important feature in their design is the use of the rigid pentiptycene group, which can prevent interchain π -stack of polymer backbones and thus reduces self-quenching of luminescence and imparts a large free volume for trapping analyte molecules.

As we reported previously, fluorescent polymers containing the pendent cholesteryl ester groups also show rapid and large response to DNT vapor³⁹ (Figure I.5). The polymers were prepared by the Suzuki cross-coupling reaction of dibromide and bisboronic acid ester monomers. Dibromide monomer was readily derived from dibromoterephthalate by introduction of the large cholesteryl groups. The bulky cholesteryl esters act as a site-isolating group to prevent the interchain interaction and create a large free volume in the polymer solids, which therefore results in high fluorescence quantum efficiency and easy trapping of the analyte molecules. The polymers are easy to prepare, structurally simple for variation and modification, and highly fluorescent.

Figure I.5. Fluorescent polymers containing the cholesteryl ester groups

Based on Swager's and our work, a new conjugated polymer (**P1**) containing both the rigid pentiptycene and bulky cholesteryl ester groups is designed, aiming at a high sensitivity in detection of nitroaromatic explosives and other electron-deficient analytes (e.g., isocyanates). The phenylene-acetylene backbone in **P1** ensures the effective conjugation for the exciton migration in the excited state. The pentiptycene and pendent cholesteryl ester groups serve to prevent the interchain interaction and provide a large cavity in bulk polymer.

Polymer **P1** can typically be synthesized by the Sonogashira cross-coupling reaction with a high yield (Scheme I.1). The pentiptycene-diacetylene monomer is known, while the dibromide monomer can be readily derived from dibromoterephthalic acid by esterification with cholesterol.

Scheme I.1. Synthesis of conjugated polymer **P1**

Figure I.6. Structure of polymer **P2**

The sensing property of polymer **P1** will be studied through the fluorescence quenching experiments using DNT and isocyanates as analytes under various experimental conditions. Another conjugated polymer (**P2**) will also be used in isocyanate detection (Figure I.6). A comparison of **P1** and **P2** for detection of vapors of DNT and isocyanates should then be made, in order to understand more the structure-sensing property of this type of fluorescent conjugated polymers. Accordingly, the overall objectives of this thesis work are:

(1) to synthesize and characterize conjugated fluorescent polymer **P1**,

- (2) to characterize the sensing properties of polymer **P1** towards DNT using standard lab fluorimeter and optic-fiber probe,
- (3) to study the effect of film thickness and compositions on the sensing properties, and
- (4) to explore the detection of isocyanate vapors using polymers **P1** and **P2**.

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CHAPTER II

Synthesis and Characterization of Monomers and Polymer

II.1 Overview of Sonogashira Cross-coupling Reaction

Nowadays, transition-metal-catalyzed cross-coupling reactions have become a powerful tool in organic synthesis¹⁻⁵. Among them, the palladium-catalyzed sp^2 - sp coupling reaction between an aryl or alkenyl halide or triflate and a terminal alkyne, has become the most important method to prepare aryl alkynes and conjugated alkynes, which are precursors for natural products, pharmaceuticals, and molecular organic materials, and are widely used in fluorescent conjugated pre-polymers and polymers⁶⁻⁸ (Scheme II.1). In the earlier studies, such reactions were catalyzed by a phosphane-palladium complex and using triethylamine or sodium methoxide as base and piperidine or DMF as solvent. However, these reactions generally required high temperature (up to 100 °C). In 1975, Kenkichi Sonogashira and Nobue Hagihara found that the addition of a catalytic amount of copper(I) iodide can greatly accelerate the reaction, thus enabling performance of the alkynylation at room temperature. This new reaction came to be known as the Sonogashira-Hagihara protocol (more often simply known as Sonogashira coupling) and has since become the most popular procedure for the alkynylation of aryl or alkenyl halides⁹. Syntheses of cross-conjugated oligo(phenylene enynylene)s and phenanthroline derivatives^{10,11} are a few examples.

Scheme II.1. The Sonogashira cross-coupling reaction

Generally, the Sonogashira reaction is a coupling reaction of terminal alkynes with aryl or vinyl halides. Two catalysts are needed for this reaction: a zero-valent palladium complex and a halide salt of copper(I). The reaction medium must be basic to neutralize the hydrogen halide produced as the by-product of this coupling reaction, employing alkylamines such as triethylamine and diethylamine sometimes as solvents. Meanwhile, the reaction system needs to be oxygen-free because the palladium(0) complexes are unstable in air, and oxygen promotes the formation of homo-coupled acetylenes.

Although there is still doubt of the mechanism of the Sonogashira coupling reaction, the reaction is believed to take place through two independent catalytic cycles as shown in Scheme II.2, the palladium cycle and copper cycle. The active palladium catalyst is the 14-electron compound $\text{Pd}(0)\text{L}_2$ (complex **A**), (L represents ligand) which reacts with the aryl halide or triflate by oxidative addition to $\text{Pd}(\text{II})$ (complex **B**). Phosphine-palladium complexes such as tetrakis(triphenylphosphine)palladium(0) are used for this reaction, but palladium(II) complexes are also available because they are reduced to the palladium(0) species by the consumption of terminal alkynes in the reaction medium. Complex **B** reacts in a rate limiting transmetalation step with the copper acetylide produced in the copper cycle to complex **C** expelling the copper halide CuX (complex **G**) (X represents halogen). Both organic ligands are *trans* oriented and convert to *cis* in a trans-cis isomerization to complex **D**. In the final step, the product is released by reductive elimination with regeneration of the catalytic $\text{Pd}(0)$. In contrast, copper(I) halides react with the terminal alkyne and produce copper(I) acetylide, which acts as an activated species for the coupling reactions.

Scheme II.2. Sonogashira reaction mechanism

For this type of alkylation procedure, the general reactivity order of the sp^2 species is vinyl iodide $\geq$ vinyl triflate $>$ vinyl bromide $>$ vinyl chloride $>$ aryl iodide $>$ aryl triflate $\geq$ aryl bromide $\gg$ aryl chloride. Therefore, the Sonogashira reaction process usually runs smoothly when the more expensive and unstable aryl or vinyl iodides are used.

Moreover, if the organic halide system is “activated”, that is, electron-poor, the reaction is even more favourable¹². Thus, the cheapest aryl chlorides, if not strongly activated, are not well-suited to the cross-coupling methodology.

II.2 Synthesis of Polymer P1

The synthetic route to the pentiptycene diacetylene **7** is outlined in Schemes II.3 and II.4. Compound **7** was prepared in six steps^{13,14}, starting from the commercially available anthracene (**1**) and p-benzoquinone (**2**). Triptycene monoquinone **3** was prepared by a one-step reaction of anthracene (**1**) and excess benzoquinone (**2**) in acetic acid with a yield of 94% (Scheme II.3).

Scheme II.3. Synthetic route to compound **4**

If the same method was used to synthesize compound **4**, a complex mixture of products would be obtained, because 1) the excess benzoquinones used could complicate the reaction; 2) the oxidative capacity of the triptycene quinone is weaker than that of the benzoquinone, which tends to give a low yield or semiquinone as a by-product. Considering that excess benzoquinones only act as oxidants, p-chloranil, a stronger oxidant, was then used instead of the excess quinones in the one-pot method for the synthesis of compound **4**. This synthetic protocol was proved correct and effective in that the reaction of 1 equiv of triptycene quinone **3** with anthracene in refluxing acetic acid in the presence of 1 equiv of p-chloranil afforded pentiptycene monoquinone **4** in 90% yield (Scheme II.3).

Scheme II.4. Synthetic route to compound **7**

Compound **5** was prepared in a two-step reaction. Lithium trimethylsilylacetylnide was obtained first by adding 1 equivalent of *n*-butyllithium to a solution of (trimethylsilyl) acetylene in THF at 0 °C. Nucleophilic addition of lithium trimethylsilylacetylnide to quinone **4** was performed in THF at 0 °C, and the mixture was slowly warmed up to room temperature and stirred overnight. Compound **5** was obtained with more than 90% yield. Reductive aromatization of the central ring produced the trimethylsilyl-protected diethynylpentiptycene **6** with a yield of 82%. Deprotection of the TMS group provided the desired monomer **7**, with the total yield about 60%, with the product being light yellow and exhibiting poor solubility in organic solvents (Scheme II.4).

Scheme II.5. Synthetic route to dibromo monomer **11**

Dibromo-diester monomer **11** was prepared in three steps from 1,4-dibromo-2,5-dimethylbenzene (**8**) (Scheme II.5). Compound **8** was oxidized using excess potassium permanganate in aqueous pyridine to give compound **9** with high yield of 95%. Both free radicals and the special activity of the benzylic position play a role in the reaction of alkylbenzenes with KMnO_4 to give benzoic acids. Side chains are “chewed down” to carboxylic acids regardless of their length. In order for the reaction to proceed, there must be at least one hydrogen in the benzylic position. The mechanistic details are not well known, but the reaction is believed that under basic conditions MnO_4^- ions form the “manganate esters” with alcohols in aqueous solution. The esters decompose by elimination of HMnO_3 to yield the carboxylic acid group in the final product¹⁵.

Although this reaction needs excess oxidizing agent which must be added group by group and takes time, the reaction can be completed with a yield of over 90%. Compound **9** was isolated and analyzed by ^1H and ^{13}C NMR and no trace of $-\text{CH}_3$ was found in the product. Considering the reactivity of carbonyl derivatives to esterification, compound **10** was designed here instead of directly using the carboxylic acid **9**. The hierarchy of reactivity is as follows:

This order is partly due to how good the leaving group is (acid chloride is the best) and partly due to how the good nucleophile needed to make the derivative (carboxylic acid is the best). The general trend is that good nucleophiles are poor leaving groups, thus low reactivity¹⁷. With the reactivity in mind, we converted 2,5-dibromoterephthalic acid

into an acid chloride (compound **10**) in 100% yield. The reaction mechanism is shown below.

Scheme II.6. Mechanism of acylation

Thionyl chloride reacts with the OH group of a carboxylic acid turning it into a good leaving group, producing the acyl chloride intermediate.

Esterification with cholesterol gave compound **11** in 58 % yield. Acid chlorides are particularly reactive in S_N2 reactions as the chloride ion is a very good leaving group. The added tetraalkylammonium chloride salt is a phase transfer catalyst that has a polar group (N^+) and hydrocarbon side chains. These long chains keep the $BnEt_3N^+RO^-$ ion pairs being soluble in organic phase during the reaction. The ammonium salt also acts as a basic catalyst for the reaction (Scheme II.7).

Scheme II.7. Mechanism of esterification

The Sonogashira cross-coupling reaction between pentiptycene diacetylene **7** and dibromo-diester **11** catalyzed by palladium(0) and copper(I) gave polymer **P1** in 87.5% yield (Scheme II.8).

Scheme II.8. Synthesis of polymer **P1**

II.3 Characterization of Monomers and Polymer P1

The chemical structure of the monomers and polymer were verified by NMR and IR spectroscopy. ^1H and ^{13}C assignments were done with the aid of COSY and HETCOR experiments. The IR spectroscopy was used to identify the characteristic carbonyl band in the range of $1716\text{--}1734\text{ cm}^{-1}$. Monomers and **P1** show high solubility in common organic solvents, such as chloroform, toluene and tetrahydrofuran. The apparent molecular weight and polydispersity were determined by gel permeation chromatography (GPC). The inherent viscosity was determined using Ubbelohde viscometer (size OB114) in 0.5 % (g/dL) chloroform solution at $30\text{ }^\circ\text{C}$. Decomposition temperature of polymer was measured by thermogravimetric analysis (TGA), and glass transition temperature of polymer was measured by differential scanning calorimetry (DSC).

II.3.1 Characterization of Monomers

NMR analyses were performed for monomers **7** and **11** plus all the synthetic intermediates. ^1H NMR and ^{13}C NMR assignments were done with the aid of COSY and HETCOR experiments. Due to the low solubility of monomer **7**, the ^{13}C NMR spectrum

could not be obtained. For monomer **11**, because of overlapping in the aliphatic proton region, only the vital peaks for identification were assigned. The ^1H and ^{13}C NMR data of monomers **7** and **11** are listed in Table II.1 and their spectra are shown in Figures II.1, II.2 and II.3. The spectra of other intermediates are shown in Figures A.1 to B.2 in the appendices. The ^1H NMR spectrum of monomer **7** showed one singlet for the $\text{CH}\equiv\text{CH}$ protons (δ 3.69), and one singlet for the bridgehead 4 protons (δ 5.82) connected to the benzene rings. The ^1H NMR spectrum of monomer **11** showed a multiplet peak (δ 4.92) assigned to the proton (**H2** shown in Table II.1) on the α -C adjacent to the ester bond, and the missing of the multiplet peak (δ 3.49) assigned to the proton adjacent to the hydroxyl group in cholesterol indicating the formation of the ester bond. Furthermore, all the peak integrals are in correct ratios according to the expected structures of the monomers.

Table II.1. ^1H and ^{13}C NMR assignments of monomers **7** and **11**

Compounds	^1H ^{13}C	δ , ppm
H1 H2 H3 H4	6.95 7.36 5.82 3.69
C1 C2 C3 C4 C5 C6 C7 C8	125.7 123.7 145.7 48.7 144.1 120.9 82.3 85.6
H1 H2 H3 H4 H5 H6 H7 H8	8.00 4.92 2.52 5.49 1.14 0.71 0.91 0.87
C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11	136.03 136.25 119.98 163.77 123.19 139.22 76.47 19.36 11.87 18.73 22.58

[illegible]

Figure II.2. ^1H NMR (300 MHz, CDCl_3) spectrum of monomer **11**

Figure II.3. ^{13}C NMR (75 MHz, CDCl_3) spectra of monomer 11

The absorption and fluorescence spectra of monomer 7 and 11 were measured in their chloroform solution. The results are shown in Figure II.4. Diacetylene monomer 7 displays absorption with maximum wavelength at 332 nm. By excitation with 330-nm

light, it emits around 325-425 nm. Dibromo-diester monomer **11** has a strong absorption with the maximum wavelength at 306 nm, while it shows almost no emission with excitation at 306 nm.

Figure II.4. Absorption and fluorescence spectra of monomers **7** (dashed lines) and **11** (solid lines) in chloroform solutions

II.3.2 Characterization of Polymer P1

Spectroscopic Analysis

The IR analysis was done on thin film of polymer **P1**, which was cast on the NaCl plate. The pendent ester groups give an intense C=O band in the range of 1716-1724 cm^{-1} (ref. 19, 1715-1740 cm^{-1}), slightly red-shifted due to the conjugation with the phenyl group. The C $\equiv$ C band at 2202 cm^{-1} , C=C band at 1458 cm^{-1} and sp^2 aromatic C-H and sp^3 aliphatic bands in the range of 2869-3006 cm^{-1} were also observed. Polymer **P1** was

characterized by ^1H and ^{13}C NMR spectroscopy (Table II.2, Figures II.5 and II.6). Only important peaks that are vital to the identification of its structures were assigned.

Table II.2. ^1H and ^{13}C NMR assignments of polymer **P1**

P1	^1H NMR	δ, ppm
H1 H2 H3	7.03 7.57 5.50
P1	^{13}C NMR	δ, ppm
C1 C2 C3 C4 C5 C6 C7 C8	125.35 123.22 145.14 50.06 144.99 99.30 139.33 136.26

1D proton

Figure II.5. ^1H NMR (300 MHz, CDCl_3) spectrum of **P1**

Figure II.6. ^{13}C NMR (75 MHz, CDCl_3) spectrum of P1

Molecular Weight

Optical, thermal and mechanical properties of polymers are all dependent on the molecular weight. In general, as the molecular weight increases, physical properties improve until they reach a plateau value at which point further increase in the molecular weight will have only limited effect on the properties. Photophysical properties follow the same rules, not only the wavelength of absorption and emission, but also the fluorescence efficiency. Typically, as a fluorescent sensor, polymers of higher molecular weight have a long effective conjugation length, thus a long effective length for energy

transfer¹⁸. The molecular weight of polymer **P1**, as determined by GPC relative to polystyrene standards, was 100000 with the polydispersity index of 3.0.

Solution viscosity was used to estimate the molecular weight of polymer **P1**. One of the most characteristic features of a dilute polymer solution is that its viscosity is considerably higher than that of a pure solvent¹⁶. Generally, when comparing polymers with similar structures, the higher viscosity affords the higher molecular weight. The inherent viscosity value of polymer **P1** is 0.92 dL/g at 30 °C, being higher than 0.5 dL/g for most polymers with similar structures and thus indicative of high molecular weight.

Thermal Analysis

For use in a chemosensor, the thermal stability of **P1** should also be considered as it could be used at the elevated temperatures. TGA is a standard method in which the changes in the weight (mass) of a sample as a function of temperature and/or time can be measured²¹. The decomposition temperature (Td) of **P1** is above 288 °C in nitrogen (5% weight loss, at a heating rate of 10 °C/min). The relatively low decomposition temperature of the polymer is due to the presence of the aliphatic cholesteryl ester groups. DSC is often used to measure the phase transitions at a given temperature of the polymer sample, such as the glass transition and crystallization temperatures²⁰. When a polymer undergoes a phase transition, its optical property can change significantly. Likely due to the rigid polymer backbone and the bulky pendent groups, the glass transition temperatures (Tg) of **P1** was not observed up to 290 °C prior to its thermal decomposition.

Photophysical Property

The absorption and fluorescence spectra of **P1** were taken in chloroform solution and as solid film (Figure II.7 and Table II.3). The polymer displays a strong absorption band which arises from π - π^* transition and strong blue-green fluorescence. Except for a small red shift, a good spectral match between the solution and thin film samples indicates that the polymer does not aggregate nor much interchain interaction. It can be also observed from the minimal difference in the shapes of the polymer film and solution spectra. The small red shift may be due to the conversion of conformation in solid-state. The quantum yield in solution relative to quinine sulfate is 0.68. The absolute fluorescence quantum yield of **P1** film was measured to be 0.30 using an integral sphere.

Considering the use in a fiber-optic sensing system, the emission spectra were then compared between **P1** film spin-coated on glass plate and optic-fiber tip (Figure II.8). The slight broadening in the PL emission for the film coated on the fiber is deemed not to affect the sensing experiments; therefore, any changes in the fluorescence signals of polymer upon exposure to vapor analyte can be detected via the optic-fiber probe.

Table II.3. Photophysical property of polymer **P1**

	Abs $\lambda_{\max}$ (nm)	PL $\lambda_{\max}$ (nm)	Φ_F^a
Solution ^b	429	452	0.68
Solid ^c	453	479	0.30

^a Quantum yield of solution in chloroform and absolute fluorescence efficiency of thin film. ^{b, c} Absorption and photoluminescence were measured in chloroform and film (5 nm) with excitation at 390 nm.

Figure II.7. Absorption and fluorescence spectra of **P1** in chloroform (solid lines) and in spin-coated films (dashed lines)

Figure II.8. Fluorescence spectra of **P1** film coated on glass plate (solid line) and on optic-fiber (dash-dotted line)

II.4 Fluorescence Property of Polymer P2

Polymer **P2** is a conjugated polymer containing fluorene and phenylene in the backbone. **P2** was prepared in our group before²⁵ and shown to be a good sensory material for DNT detection²³. Polymer **P2** was used mainly for comparison with polymer

P1 in this work in order to see which part of the structure in the repeat unit contributes more or less to the sensing performance.

Scheme II.9. Synthetic route to polymer **P2**

A general synthetic route to polymer **P2** is outlined in Scheme II.9. Monomer **12** was prepared by acid-catalyzed esterification of 2,5-dibromoterephthalic acid with methanol with high yield. Bisboronic ester monomer **13** is readily available from a commercial source. The Suzuki cross-coupling reaction of monomer **12** with monomer **13** afforded polymer **P2**. Polymer **P2** is completely soluble in common organic solvents, such as toluene, THF, DMF, and chloroform. The molecular weight is determined by GPC ($M_w = 5.06 \times 10^4$, PDI = 4.62). As shown in Figure II.9, the absorption spectrum of polymer **P2** displays one band at 355 nm^{26,27}. Excitation of its thin films at 350 nm led to the emission of blue color with the maximum peak at 455 nm. Absolute fluorescence quantum efficiency of **P2** film is 0.46.

Figure II.9. Absorption (dotted line) and emission (solid line) spectra of **P2** film (excited at 350 nm)

In comparison with **P2**, the synthetic route to **P1** is longer. Although it has a high molecular weight and can form high-quality thin films, **P1** has lower absolute quantum yield than **P2**. Films of **P1** and **P2** emit blue color with the maximum wavelength at 479 nm and 455 nm, respectively.

II.5 Conclusion

A new fluorescent polymer having pentyptycene moiety in the polymer backbone and cholesteryl esters as pendent groups was successfully synthesized by the Sonogashira cross-coupling. The two key monomers were prepared in at least 9 steps, starting from readily available anthracene, benzoquinone and 1,4-dibromo-2,5-dimethylbenzene. In comparison with a known polymer **P2**, polymer **P1** should also be a good candidate as a fluorescent sensory material for detection of explosives and possibly other chemicals.

II.6 Experimental Section

II.6.1 Materials

Tetrahydrofuran and toluene (from Aldrich) were dried by refluxing over a bed of sodium and benzophenone. Other reagents and solvents were purchased as a reagent grade from Aldrich Canada Inc. and used without further purification. Macherey-Nagel precoated TLC plates (silica gel 60 G/UV254, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel (Silicycle Chemical Division, 0.04-0.06 μm , 230-400 mesh) was used as the stationary phase for column chromatography.

II.6.2 General Characterizations

^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Advanced Digital NMR 300 spectrophotometer, and chemical shifts are reported in ppm relative to TMS in proton spectra and carbon spectra. Mass spectrometry was obtained by the Micromass Quattro LC ESI instrument. Infrared measurements were performed on a Varian 1000 FT-IR Scirntar series spectrophotometer. The molecular weight of polymer was determined by using a PL gel 5μ column and a UV absorbance detector at 254 nm at a flow rate of 1.0 mL/min in CHCl_3 . The molecular weight was reported relative to polystyrene standards purchased from Polysciences, Inc. with $M_w/M_n = 1.04$. Inherent viscosity data were obtained with Ubbelohde viscometer (size OB114) in 0.5 % (g/dL) chloroform solution at 30 $^\circ\text{C}$. Decomposition temperature of product were measured on a Thermogravimetric Analyzer (TGA) 2950 CE Instrument at a heating rate of 10.00 $^\circ\text{C}$ /min. Polymer films on glass plates (microscope slide, 20 x 20 x 1 mm) were spin-coated by a Chemat Technology Spin-Coater KW-4B, using a spin-rate of 1500 rpm from chloroform

solutions, and stored in the dark overnight before use. UV-vis spectra were recorded using a UV-vis-NIR Lambda 900 spectrophotometer, while the fluorescence studies were made with a Shimadzu RF-1501 spectrofluorophotometer. Polymer thin-film spectra were recorded by front-face (34° angle) detection. Fluorescence quantum yields in chloroform solution were determined relative to an equiv-absorbing solution of quinine sulphate, while absolute quantum yield of polymer film was measured by using integrated sphere.

II.6.3 Film Preparation

Polymer films were spin-coated on glass plate (microscope slide, 20 x 20 x 1 mm) from chloroform solution. Generally, to prepare a 10-nm thick film, it requires 1 mg of polymer in 10 mL of chloroform. The films were dried in air overnight before use. The film thickness was measured by Atomic Force Microscopy (AFM) (uncertainty: ± 0.2 nm) and found to range from 2 – 65 nm.

II.6.4 Syntheses

9,10-Dihydro-9,10-*o*-benzenoanthracene-1, 4-Dione (3)

A mixture of anthracene (**1**) (3.2 g, 18.0 mmol) and *p*-benzoquinone (**2**) (10.8 g, 100 mmol) in acetic acid (150 mL) was refluxed for 3 h. The reaction mixture was then poured into water, and the precipitate was filtrated. The crude product was washed with hot water and purified by column chromatography with chloroform solvent. The yellow solid was rotor-evaporated and dried to give 4.788 g (94% yield) of product. **3** (mp 294.0 °C, lit.²² mp 292-296 °C): ¹H NMR (300 MHz, CDCl₃) δ 6.60 (s, 2H), 5.80, (s, 2H), 7.43 (m, 4H), 7.04 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 135.36, 183.48, 151.90, 47.36, 143.57, 124.40, 125.56.

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzeno)pentacene-6,13-dione (4**)**

A mixture of 4.6 g (16.2 mmol) of compound **3** and 2.881 g (16.2 mmol) of anthracene (**1**) and 3.983 g of *p*-chloranil in 250 mL of HOAc was refluxed for 24 h. The resulting mixture was cooled to room temperature. The precipitate was filtered, washed with ether, and then dried in air to give 6.71 g (90 % yield) of **4** as a yellow solid. **4** (mp >350 °C, lit.²² mp > 370 °C): ¹H NMR (300 MHz, CDCl₃) δ 5.77 (s, 4H), 6.97 (m, 8H), 7.36 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 125.46, 124.24, 143.65, 47.39, 150.95, 179.96.

Compound 6

Under an atmosphere of argon, 14.6 mL (36.14 mmol, 1 equiv) of *n*-butyllithium (2.5 mmol) in hexane was added dropwise to a solution of (trimethylsilyl)acetylene (5.1 mL, 36.14 mmol, 1 equiv) in THF (50 mL) at 0 °C. The mixture was then kept at 0 °C for another 40 min before it was transferred to a solution of quinone (**4**) (6.7 g, 14.56 mmol, 2.5 equiv) in THF at 0 °C. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with 5 mL of water and then subjected to a CHCl₃/H₂O workup. The solvent was removed and the residue was precipitated in hexane. The resulting white solid (8.6 g, 90%), which is a mixture of the trans- and cis-isomers, was collected by filtration.

Crude compound **5** (8.6 g, 13.12 mmol) was dissolved in 250 mL of acetone and then a solution of tin(II) chloride dihydrate (7.12 g, 31.4 mmol) in 50% of acetic acid (100 mL) was added dropwise. This mixture was stirred at room temperature for another 24 h and the resulting solid product was filtered. The solid was dissolved in CHCl₃ and washed with water and then sodium bicarbonate solution twice and dried with MgSO₄. The CHCl₃ was removed by rotor-evaporation and the residue was washed with hexane. The resulting white solid was dried in air and collected (6.69 g, 82.2% yield). **6** (mp 417 °C, lit.¹³ mp 419 °C): ¹H NMR (300 MHz, CDCl₃) 0.51 (s, 18H), 5.80 (s, 4H), 6.96 (m, 8H),

7.36 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) 0.31, 52.2, 100.7, 102.5, 114.8, 123.8, 125.2, 144.1, 144.9.

Compound 7

Compound **6** (6.69 g) was dissolved in a mixture of THF (150 mL) and methanol (150 mL). A solution of KOH (5 g in 15 mL of H_2O) was added and the mixture was stirred at room temperature for 5 h. The resulting solid product was filtered and washed with water, methanol and hexane. After dried in vacuum, light yellow product was obtained (3.1 g, 60% yield). **7** (mp 437 °C, lit.¹³ mp 439.5 °C): ^1H NMR (300 MHz, CDCl_3) 3.69 (s, 2H), 5.82 (s, 4H), 6.95 (m, 8H), 7.36 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) 125.7, 123.7, 145.7, 48.7, 144.1, 120.9, 82.3, 85.6.

2, 5-Dibromoterephthalic acid (**9**)

1,4-Dibromo-2,5-dimethylbenzene **8** (3.00 g, 11.4 mmol) in pyridine (70 mL) and water (20 mL) containing 7.0 g of KMnO_4 was refluxed for 2 h. Then, in every 30 min, 5 mL of water containing 2 g of KMnO_4 was added, which was repeated 8 times. After 5-6

h, 20 mL of water was added and the purple mixture was refluxed overnight. The brown residue (MnO_2) was filtered through Celite while hot and washed with boiled water. The filtrate was rotor-evaporated to remove most of water and pyridine. Drops of concentrated H_2SO_4 were added to get white precipitate. The solid was dried in air and the product can be obtained over a yield of 80%. **9** (mp 315 °C, lit.²⁴ mp 318 °C): ^1H NMR (300 MHz, DMSO-d_6) δ 13.95 (s, 2 OH), 8.046 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 137.5, 135.4, 119.2.

Bis(10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 2,5-dibromoterephthalate (11)

2,5-Dibromoterephthalic acid (**9**) (2.42 g, 7.47 mmol) and thionyl chloride (30 mL) were added to round-bottom flask which was dried in oven overnight and heated to a reflux for at least 3 h (completely dissolved). Thionyl chloride was rotor-evaporated to give 2,5-dibromoterephthaloyl dichloride **10** in 100% yield. Under argon atmosphere, to a solution of cholesterol (2.17 g, 5.6 mmol) and **10** (0.50 g, 1.4 mmol) in toluene (50 mL), benzyltriethylammonium chloride (0.22 g, 10% mole) was added. The mixture was heated at 90 °C and stirred overnight. The reaction mixture was cooled to room temperature, ethyl acetate was added and the precipitate was collected. After dissolved in chloroform, filtered to remove residue and purified by column (chloroform: hexane,

2:1.5) white solids were obtained (0.86 g, 58 % yield). **11** (mp 252-253 °C, lit.²³ mp 259-261 °C): ¹H NMR (300 MHz, CDCl₃) δ 8.00 (s, 2H), 5.46 (s, 2H), 4.91 (m, 2H), 2.52 (d, 4H), 2.03-0.72 (m, 82H); ¹³C NMR (75 MHz, CDCl₃) δ 163.77, 139.22, 136.25, 136.03, 123.19, 119.97, 56.68, 56.13, 50.01, 45.80, 42.32, 39.71, 39.52, 37.97, 36.96, 36.63, 36.19, 35.81, 31.93, 31.85, 28.24, 28.03, 27.72, 24.30, 23.84, 22.84, 22.58, 21.06, 19.36, 18.73, 11.87, 8.63.

General Procedure for Polymerization

Under an atmosphere of argon, diacetylene monomer **7** (0.1243 g, 0.260 mmol), dibromide monomer **11** (0.2759 g, 0.260 mmol), Pd(Ph₃)₄ (0.040 g, 0.0344 mmol) and CuI (0.040 g, 0.212 mmol) were added to a 25 mL, two-necked round-bottomed flask, followed by addition of anhydrous toluene/diisopropylamine (3:2, 10 mL). The mixture was purged with argon for another 10 min and then heated at 65 °C for 3 days. The reaction mixture was diluted with CHCl₃ and washed with water at least 3 times. The organic phase was further washed with aqueous NH₄Cl solution twice and then dried over anhydrous MgSO₄. The solvent was removed in vacuo and the residue was reprecipitated in methanol three times. The resulting polymer was collected and dried in vacuo (0.350 g, 87.5% yield). IR (film, cm⁻¹): 2203 (C≡C), 1724 (C=O, ester), 1458 (C=C); ¹H NMR (300 MHz, CDCl₃): 8.48 (s, 1H), 7.19 (m, 8H), 6.88 (m, 8H), 5.37 (m, 2H), 5.19 (s, 4H), 3.99 (m, 2H), 2.55-0.9 (m, 90H); ¹³C NMR (100 MHz, CDCl₃): 165.9, 145.7, 144.1, 140.8, 126.7, 123.7, 120.9, 99.3, 95.4, 93.3, 80.9, 73.7, 49.7, 37.4, 23.2.

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CHAPTER III

DNT Vapor Detection

III.1 Preparation of Polymer Films

Both polymers **P1** and **P2** are considered to be a good sensory material for explosive detection, because they contain the electron-rich groups to interact or attract the electron-deficient nitroaromatics, have strong fluorescence transduction signals and are able to form high-quality films. Apart from the structural and optical properties of the polymer, the diffusion process of the analyte through a polymer film, the thickness and morphology of films can affect the detection sensitivity and selectivity as well. Considering these factors, films of **P1** with different thickness and modifications were then prepared to probe the effect of the polymer film thickness and composition on the sensing property for detection of nitroaromatic explosives.

Experimentally, we explored the use of a thin layer of (3-aminopropyl)triethoxysilane (APTES) as undercoating for the polymer **P1** film, varied the film thickness, and blended **P1** with another polar polymer (polystyrene-maleic anhydride copolymer, PSMA). After studying the effect of various parameters, detection of DNT was demonstrated using the polymer **P1** coated on glass plate and then on the optic fiber tip.

Films Coated on Glass Substrate by Casting and Spin Coating

Polymer films were spin coated from chloroform solutions onto microscope slide (length = 20 mm, width = 20 mm, thickness = 1.0 mm) and then slowly dried in dark at room temperature overnight. The polymer solutions in concentration ranging from 0.025 to 10 mg/mL in chloroform were used to prepare the films in 2-100 nm thickness. Using a Chemat KW-4B Spin-Coater, drops of polymer solution were placed on the glass plate and then spun at 1500 rpm.

Film Coated on Fibers by Dip Coating

Films for fiber sensing were dip-coated from chloroform solutions. A typical procedure is as follows: one drop of the polymer solution is dispensed onto the side wall of a fiber (15-cm long and 800- μ m core). Drying is done in dark under ambient temperatures for at least 2 hours. The thickness of the polymer coating varies from 30 to 110 nm. The film uniformity is not strictly controlled.

III.2 Detection of DNT Using Films Coated on Glass Plate

The setup for DNT sensing is simple to assemble, convenient to use and reliable to quickly screen the polymer samples. Polymer film was exposed to the vapor of DNT powders that were placed at the bottom of 20 mL vial and covered with cotton gauze at room temperature. The fluorescence spectra were recorded immediately after exposing the polymer film to the analyte vapor for a specific period and then excited at 390 nm. DNT was used as an analyte in our study, because of its higher equilibrium vapor pressure (1.47×10^{-4} mmHg at 22 °C) than TNT (8.06×10^{-6} mmHg at 25 °C).

DNT Quenching Study

Figure III.1 shows the time-dependent fluorescence intensity of the **P1** film (5 nm) upon exposure to DNT vapor. The fluorescence intensity dropped 48.5% at 60-s and 75.4% at 300-s.

Figure III.1. The time-dependent PL spectra (excitation at 390 nm) of **P1** (spin-coated film 10 nm) upon exposure to DNT vapor at room temperature at 0, 30, 60, 120, 180 and 300s. Inset: Fluorescence quenching response over time

III.3 Effect of Film Thickness

The thickness of polymer film relates to the time for analyte molecules to diffuse into the film, which in turn relates to the number of energy traps available in the entire polymer film or the fluorescence quenching response of a given sensory polymer film. Therefore, it is important to study and optimize the thickness of polymer film.

Films of polymer **P1** in thickness from ca. 2 nm to 70 nm were spin-coated on glass plates from chloroform solution in different concentrations and then subjected to the PL quenching tests under the same environmental conditions. The fluorescence quenching response (FQR, ΔPL %) is defined as

$$\Delta PL\% = (I_0 - I)/I_0 \times 100\%,$$

where I_0 and I are the fluorescence intensity prior to and after exposure to analyte (DNT) vapor, respectively.

The FQR at different times to the same analyte are shown in Figures III.2 and III.3. In a 2-3 nm film, the FQR at 30-s exposure is 35.3%; however, it reduces to only 10.3 % with a film in 58-62 nm thickness. The similar results were observed at all the other time intervals within 60-s exposure to DNT vapor: thinner films give a higher response, especially in the first 30 seconds. The results indicate that the more DNT molecules can diffuse into the thinner film than the thicker films for a given time within 60 seconds and the film thickness of 2-3 nm is the best in our case for sensing with the largest FQR (e.g., 15-52%) and the shortest time (e.g., 10-60 s). A similar pattern can be found within 1-5 minutes of DNT exposure (Figure III.3). However, after 5 minutes of exposure to DNT, films around 5-25 nm thickness gave almost the same FQR (75.1-75.5%), which means that the concentration of analyte molecules in the film, regardless the film thickness, has reached the equilibrium. Due to the limited distance of diffusion of analyte in thick films in a short time, there is always a layer of film close to the substrate whose PL cannot be quenched (Scheme III.1), and as well the large FQR may offer a high detection sensitivity is in trade-off with a long detection time (>5 min). Therefore, it is desirable to use a thinner film for sensing nitroaromatic vapor.

Figure III.2. Fluorescence quenching response of films of **P1** in different thickness after 10-60 seconds of exposure to DNT vapor

Figure III.3. Fluorescence quenching response of films of **P1** in different thickness after 1-5 minutes of exposure to DNT vapor

Scheme III.1. Illustration of film thickness effect on the fluorescence quenching displayed by nitroaromatics

III.4 Effect of Undercoating

The concentration of analyte molecules in the sensory polymer film also depends on the interaction between the polymer and analyte. The polar electron-donating groups such as amino tend to bind to the electron-deficient nitroaromatic compounds through the electron donor and acceptor interaction. Thus, it is conceivable that the addition of the amino-containing component into a sensory polymer can help ‘fix’ the nitroaromatic in the sensory film and thus increase the analyte concentration or enhance the FQR.

APTES is a surface promoter for a variety of substrates such as glass, silicone and plastics and can form an ultrathin layer containing the amino group on the surface. In our work, APTES was spin-coated on the glass plate from its 2% solution in toluene, and heated at 120 °C for 10-15 minutes to form a thin layer of undercoating (7.5-8.5 nm). The **P1** films were then spin-coated on the APTES-treated glass plates. The films were even and smooth and the optical properties were the same as those without the APTES undercoating. The PL quenching data were collected and averaged out from six films in 5-20 nm thickness coated on glass plates with and without the APTES undercoating (Table III.1). In comparison, it is clear that the polymer films with the APTES undercoating gave a better FQR than those without the undercoating. On average, an increase of about 10-18% in FQR was achieved within 10-60 seconds. Such a noticeable improvement in detection sensitivity can be attributed to the presence of the amino-containing undercoating that is able to absorb and hold more DNT molecules in the sensory film which causes more PL quenching. We also tested the **P1** thin films with the APTES top-coating and thick films of **P1** with the APTES undercoating. Both did not give any meaningful enhancement in the FQR. For the thick film of **P1**, the PL quenching is still determined by the diffusion process of the analyte and there is no or very little interaction between the APTES coating and the analyte molecules. With the APTES top-coating, although the analyte might be adsorbed readily onto the film surface but still goes through the same diffusion path as the non-coated film, making no difference in the overall FQR. Therefore, the amino-containing undercoating can serve as a sorbent by sucking and holding the DNT molecules in the sensory film, which effectively enhances the sensing sensitivity.

Table III.1. Increase in fluorescence quenching response of **P1** films on glass plate with and without APTES undercoating

Time Thickness	Increase in Fluorescence Quenching Response (%) ^a			
	10s	20s	30s	60s
5 - 20 nm	10.9	18.5	16.3	13.0

^a Difference in FQR = $\Delta a - \Delta g$, where $\Delta = (I_0 - I)/I_0 \times 100\%$, g = glass plate; a = APTES treaded glass plate and when the FQR is at or over 50%.

III.5 Effect of Polymer Blending

By diluting a fluorescent polymer in solution or with another non-fluorescent polymer, the fluorescence quantum yield may increase due to the diminished interchain interaction. At the same time, if the non-fluorescent polymer is polar and suitable for the nitroaromatic molecules to diffuse, its blend with a sensory polymer should perform better or give a higher FQR towards the nitroaromatic analytes. Ideally, commercially available polymers should be selected for blending with polymer **P1** for potential practical application. Among many possible candidates, we selected and tested PSMA, which is a copolymer of styrene and maleic anhydride. The polar anhydride and aromatic phenyl groups in PSMA were thought to interact with the DNT analyte in our study. Three polymer blends were prepared in weight ratios of **P1**:PSMA 3:1 (75-25%), 1:1 (50-50%) and 1:3 (25-75%). The polymer blends were spin-coated on glass plates from their chloroform solutions. The fluorescent quenching response of the films of the blend and polymer **P1** in the same thickness was measured and compared. The results (Table III.2)

showed a noticeable improvement in detection sensitivity. After 2 or 3 minutes of exposure to DNT, the FQR was 16.8% larger for the blend films (3:1 ratio, 40-50 nm thickness) than the **P1** film alone. A larger increase (27.5%) in the FQR for the thicker films (50-60 nm) of polymer blend (3:1 ratio) further indicates the effect of blending with a polar polymer. The best results in terms of the FQR come from the blend with the ratio of 3:1 for **P1** and PSMA by weight. The other two blends in ratios of 1:1 and 1:3 gave less or no increase in the FQR.

Table III.2. Increase in fluorescence quenching response of polymer blend films relative to **P1** films on glass plate ^a

Time (min) \ Δ FQR (%)	Blend Film (40-50 nm)		Blend Film (50-60 nm)
	P1:PSMA (1:1)	P1:PSMA (3:1)	P1:PSMA (3:1)
1	4.2	8.8	23.6
2	6.0	16.8	27.5
3	7.8	16.8	24.1
5	6.8	18.4	18.7

^a Difference in FQR = $\Delta b - \Delta p$, where b = blend films; p = polymer films without blend

III.6 Fiber-Optic Sensing

Changes in fluorescence intensity of polymer films dip-coated on optic-fiber were determined at room temperature. Compared with the spectroscopic method using the film coated on glass plate, the optic-fiber detection is more sensitive and capable of remote sensing. The probe consists of the two fibers that bind together with one fiber serving as an excitation light delivery source and the other as a fluorescent signal collector. Polymer film is dip coated on the receiving fiber and the fluorescence signal can be efficiently transported to the monitor with a minimum loss to the surroundings.

The experimental setup is shown in Figure III.4. An Ar^+ laser beam is sent to the sensing segment via illuminating fiber (i-fiber) to excite the polymer layer. The Ar^+ laser power after i-fiber is adjusted to about 0.51 mW or lower. The polymer is coated on the side wall of the receiving fiber (r-fiber), which is excited by the coming Ar^+ laser light. The fluorescent emission is sent to the spectrometer-computer system for analysis.

Figure III.4. Schematic drawing of an experimental setup for fiber-optic sensing

DNT is placed in a small glass vial with the size of 40 mm x 50 mm. A 10 mm hole is bored in the center of the cap to allow the sensing segment to enter. Since only the vial is moving, all optical components of the sensing system remain still during the entire measurement, the signal fluctuation caused by the position change of the components is eliminated. USB 2000 is a palm-held spectrometer (Ocean Optics Inc.)

The fiber-optic sensing system has many advantages compared to the method above on glass slides; however, this system requires a minimum level of fluorescence and relatively smooth films for detection reliability. The optimal thickness (e.g., 5 nm) found for the polymer film coated on glass plate does not work well for the optic fiber probe,

due to the limitation of the required fluorescence signal. The APTES undercoating was not applied in order to simplify the coating process. It was then found that the film of polymer **P1** in 30 nm thickness is able to afford a fluorescence signal large enough for fiber-optic measurement. As shown in Figure III.5, the fluorescence intensity gradually decreases over time upon exposure to DNT vapor. A detectable change of the FQR of 25.7% was established after exposure to DNT vapor at room temperature for only 34 seconds. The 56% drop in fluorescence was observed after 2m48s. The optic-fiber detection using the blend of **P1** and PSMA also worked well. The fiber probe coated with blend film (**P1**:PSMA = 3:1 by weight, 75 nm thickness) was able to detect the DNT vapor with the additional FQR of 12.2 % at 5-min.

Figure III.5. Fluorescence quenching response of **P1** film (ca. 30 nm thickness) coated on optic-fiber tip

III.7 Comparison of Polymers **P1** and **P2**

According to the previous report⁸ and the results in this work, **P2** shows a larger and faster response upon exposure to DNT than **P1**. In both 65 nm films, the FQR of **P2** is 41% at 1-min exposure, while the FQR of **P1** is 21% with the same time of exposure. At 5-min exposure, the FQR of **P2** is 81% and the FQR of **P1** is only 38%. Polymer **P2** shows a larger PL quenching percentage and faster response for a given time. In comparison with Swager's pentiptycene polymers⁷, **P2** has the similar quenching efficiency for a given time, and the similar fluorescence quantum yield as well. However, with the consideration of the ease of synthesis, **P2** is a good candidate for optic-fiber detection of electron-deficient nitroaromatics and a sensory material for low-cost sensing system.

III.8 Conclusion

The fluorescence quenching properties of the polymer **P1** thin films in response to vapor of DNT have been investigated by varying the film thickness, applying an undercoating of APTES and blending with PSMA. A significant change in fluorescence intensity (51 % in 60-s) in response to DNT vapor exposure at ambient temperature was achieved when the polymer film coated on glass plate was about 2 nm in thickness. In comparison with the film of polymer alone, the polymer film undercoated with 7.5-8.5 nm thick APTES and the film of polymer blend containing a non-fluorescent polymer showed additional 18.5 % (in 20-s exposure) and 18.7 % (in 5-min exposure) decrease in fluorescence intensity, respectively. The use of polymer and polymer blend coated on optic-fiber tip for detection of DNT vapor has also been demonstrated.

III.9 Experimental Section

PSMA (polystyrene-maleic anhydride copolymer, $M_w = 1900$ with 75 wt% of polystyrene) was purchased from Aldrich Canada Inc. The thickness of films on both glass plate and fiber were measured by Nanosurf EasyScan Atomic Force Microscopy (AFM) and Tencor Alpha-Step 200 surface profiler.

The sensing experiment by optic fiber system is performed by following steps:

1. Turn on the OOBBase32 software to show the live spectrum from USB 2000. The fluorescent emission spectrum is recorded for freshly coated polymer before inserting it into the DNT container. The spectra are manually recorded every minute by manually switching the light on/off switch. Overlaying all these recorded spectra together in the OOBBase32 screen, the fluctuation of the signal within this period of time can be easily estimated.
2. The sensing segment is fully inserted the DNT container. Immediately the spectrum is recorded as the first quenching spectrum. This spectrum should be the same as the ones before quenching.
3. Following step 2, the spectrum is recorded. The observed fluorescent emission should drop continuously for each spectrum. Overlaying them with those before quenching, the quenching efficiency can be estimated.

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CHAPTER IV

Isocyanate Vapor Detection

IV.1 Target Isocyanates and Their Properties

Isocyanates are widely used in industry. Diisocyanates, containing the two isocyanate groups per molecule, are essential starting-materials in the production of polyurethanes (PUs)^{1,2}. PUs form one of the worlds' most popular synthetic-polymers. They are widely used as flexible foams and furnishings, coatings, adhesives, sealants and elastomers. Due to the huge demand for PUs products, diisocyanates dominate a large global market since 1960s and are produced millions of tons each year³. In the diisocyanate productions, aromatic diisocyanates account for the vast majority. Toluene diisocyanate (TDI) and 4,4'-methylenediphenyl diisocyanate (MDI) take more than 90% of the market. Other isocyanates such as p-phenylene diisocyanate (PPDI), naphthalene diisocyanate (NDI) and hexamethylene diisocyanate (HDI) are the starting materials for high-performance polyurethane materials and are produced in relatively smaller volume.

The isocyanate group reacts with water to produce carbon dioxide (CO_2) (Figure IV.1). Carbon dioxide is used as an in-situ blowing agent in order to produce polyurethane foams⁴. The isocyanate group is highly reactive with hydroxyl functional groups to form urethane linkage. When a diisocyanate reacts with a compound containing two or more hydroxyl groups (a polyol), polymer chains are formed, known as polyurethanes. The isocyanate group also reacts with the amine functional group to form urea linkage. Reaction between a diisocyanate and a compound containing two or more amine groups produces a polymer known as polyurea. The isocyanate group can react with itself in the present of catalyst. Trimerization of isocyanates can produce isocyanurates, which has high thermal stability and potential applications in the modification of polyurethanes⁵.

Figure IV.1. Some isocyanate reactions

The reactivity of isocyanates makes them harmful to human⁶. Exposure to isocyanate through inhalation and skin contact is known to result in hypersensitivity pneumonitis and occupational asthma. Exposure of isocyanates in workplace is hazardous for workers¹⁴; thermal decomposition of polyurethane products can produce isocyanates, which put firefighters in danger when there is fire in buildings⁵, since coatings of wood furniture and building insulating materials are all made of PUs. There are already safety-handling rules for isocyanate and polyurethane manufacturers in many countries, for example, by the European Diisocyanate and Polyol Producers Association⁷⁻⁹. However, there are few efficient sensors that can instantly detect isocyanates^{10,11}.

Considering the industrial mass production of isocyanates and its potential harm to people in workplace, there is an urgent need of a quick, reliable method to detect isocyanate vapors. Therefore, in this thesis work seven isocyanates were selected as target analytes in sensing experiments based on the fluorescence transduction method. As shown in Figure IV.2, they are four aromatic diisocyanates, PPDI, TDI, NDI and MDI,

and two aromatic mono-isocyanates, phenyl isocyanate (PI) and 3-chlorophenyl isocyanate (CPI), and as well one aliphatic diisocyanate, isophorone diisocyanate (IPDI). Some physical properties of some commercially available analytes are listed in Table IV.1 for comparison.

Figure IV.2. Structures of target isocyanates

Table IV.1. Vapor pressures and vapor concentrations of target isocyanates ^{a-c}

	Vapor Pressure (mmHg)	Vapor Concentration (pg/mL)	Molarity of NCO Group (mol/L)	Mw (g/mol)
TDI	<0.01	95.09	1.092	174.16
NDI	<0.001	11.48	0.109	210.20
PPDI	<0.006	52.46	0.655	160.13
MDI	4.5×10^{-6}	0.075	4.9×10^{-4}	250.56
CPI	0.3	2515.37	16.38	153.57
PI	1.4	9105.14	76.44	119.12
IPDI	0.0003	3.64	0.033	222.28

^a Vapor pressure (mmHg) data at 20 °C. The other densities are calculated based on them in vapor phase: Vapor concentration in pg/mL and the molarity of NCO group in mol/L. ^b Literatures are list in Reference 12. ^c Calculations are shown in experimental section.

IV.2 Selection of Sensory Polymers for Isocyanate Detection

In the NCO group of isocyanates, the carbon atom doubly bonded to N and O is partially positive charged. Both of N and O atoms are more electron negative than C atom and are pulling electrons away from the carbon atom through the double bond, thus making the isocyanate electron-deficient. Considering the electron-deficient nature and the vapor pressure of isocyanates, electron-rich conjugated polymers should be a candidate for sensing isocyanate vapor by the fluorescence quenching mechanism. Polymers **P1** and **P2**¹³ (Figure IV.3) show fast response in the detection of nitroaromatics and are expected to be suitable for isocyanate detection as well. Considering the relatively weaker electron-withdrawing ability of NCO functional group, adsorption and diffusion in sensory film may be weaker and slower compare to DNT. Thus, the lower fluorescence quenching may be observed in a given period. Thinner films may performance well in this case according to the result from DNT sensing study. Fluorescence quenching of **P1** and **P2** was measured using a series of isocyanates.

Figure IV.3. Structures of polymers **P1** and **P2**

IV.3 Detection of Isocyanates Using Polymer P1

The polymer films are spin-coated from chloroform solutions on glass plates and dried in air overnight before use. Changes in fluorescence intensity of polymer films were determined at room temperature. The setup for isocyanate sensing is more complicated than DNT detection, because the side-reaction of isocyanates with water can affect the results. Isocyanate samples are renewed every two days after sensing tests. Polymer film was exposed to the vapor of isocyanates at room temperature. The fluorescence spectra were recorded immediately after exposing the polymer film to the analyte vapor for a specific period and then being excited at 390 nm.

Figure IV.4. The time-dependent PL spectra (excitation at 390 nm) of **P1** film (2-3 nm thickness) upon exposure to TDI vapor at 0, 30, 60, 90, 120, 150, 180, 240, 300, 450 and 600s at room temperature at the time of 0-600s

Figure IV.5. Fluorescence quenching response of **P1** film (2-3 nm) to TDI vapor during 0-10 minutes

Figure IV.4 shows the time-dependent fluorescence intensity of thin film (2-3 nm) of **P1** upon exposure to TDI vapor. The fluorescence intensity dropped 28.47% at 60-s and 52.42% at 300-s.

The fluorescence quenching response (FQR, ΔPL %) at different times to TDI vapor is shown in Figure IV.5. In a film with thickness of 2-3 nm, the FQR at 30-s exposure was 19.1 % and at 5-min exposure was 52.4 %; however, the FQR reduced to only 25.1 % with a thicker film (25 nm). The similar results were observed at all the time intervals within 300-s exposure to the other six isocyanates. Table IV.2 shows the FQR to the vapor of seven isocyanates at 5-min exposure.

Table IV.2. FQR of **P1** film (25-30 nm thickness) to isocyanates at 5 minutes

	PPDI	TDI	NDI	CPI	PI	MDI	IPDI
FQR (%)	29.8	25.1	20.0	9.0	8.5	6.0	-

Polymer **P1** responded well to vapors of PPDI, TDI and NDI than other isocyanates, with the 20-30% decrease in fluorescence intensity. CPI and PI gave similar fluorescence quenching response around 9% and IPDI hardly quenched the PL of polymer **P1**. The observed difference in sensing sensitivity can be explained as follows. 1) The additional electron-withdrawing group in diisocyanates clearly attributes to the greater fluorescence quenching^{15,16}, in comparison with mono-isocyanates. 2) Vapor pressure (or vapor concentration) is another key factor. With higher vapor pressure, more analyte molecules are available to the sensory film, thus leading to higher fluorescence quenching. Since the vapor concentrations of PPDI, TDI and NDI (Table IV.1) are much higher than the vapor concentration of MDI, MDI gives the lowest FQR (6%) among the four diisocyanates. 3) For aliphatic isocyanates such as IPDI, because the non-conjugated isocyanate groups are not electron-deficient enough to form a donor-acceptor charge transfer^{15,16}, they are not able to quench the PL of polymer **P1**. Accordingly, the order of relative sensitivity for all the isocyanates tested towards polymer **P1** is established (Chart IV.1).

Chart IV.1. Order of relative sensitivity of isocyanates detected by polymer **P1**

As mentioned in Chapter III, film thickness affects the fluorescence quenching response for a given polymer film. The study showed that the thinner films gave a higher FQR to DNT vapor. The results indicated that film thickness of 2-3 nm is the best for DNT sensing with the largest FQR. Thus, to optimize the isocyanate sensing parameters, the films of **P1** in thickness in ca. 2 nm and 25 nm were spin-coated on glass plates and then subjected to the fluorescence quenching tests under the same environmental conditions. PPDI, TDI and NDI were used only since they gave the large and rapid quenching response. The results are shown in Figure IV.6. For each analyte, two films in different thickness (2 and 25 nm) were used. As expected, the thinner films gave a larger FQR than the thicker film. For example, upon exposure to PPDI vapor for 60-s, the FQR was 32.2% for 2-nm film but only 8.1% for 25-nm film, being nearly 3 times more sensitive.

Figure IV.6. FQR to vapors of PPDI, TDI and NDI at 60-s exposure, using **P1** films in 2 nm and 25 nm thickness

Subsequently, films in ca. 2 nm were used in experiments for sensing the three isocyanates, PPDI, TDI and NDI. In each case, the FQR reached over 50% after 300-s exposure (Table IV.3).

Table IV.3. FQR of P1 film (2-3 nm) to vapors of PPDI, TDI and NDI at given times

		PPDI		TDI		NDI	
FQR (%)	30s	18.55	30s	19.09	30s	11.53	
	60s	32.21	60s	28.47	60s	20.60	
	120s	44.02	120s	40.56	120s	36.12	
	180s	49.54	180s	46.68	180s	45.50	
	300s	56.35	300s	52.42	300s	57.61	
	600s	70.75	600s	56.01	600s	67.39	

IV.4 Detection of Isocyanates Using Polymer P2

Polymer **P2** is another ideal sensory material, which has been prepared in our group and demonstrated to have the high FQR in DNT detection. Hence, polymer **P2** was then tested to detect vapors of those seven isocyanates. The effect of film thickness was also studied.

Figures IV.7 and IV.8 show the time-dependent fluorescence intensity in thin films (2-3 nm) of **P2** upon exposure to TDI and PPDI vapors, respectively. The fluorescence intensity decreases greatly and rapidly upon exposure of the polymer film to vapors of PPDI and TDI at room temperature. At the first 10-s, the fluorescence intensity dropped 45.2% for PPDI and 23.9% for TDI. A significantly large decrease of 71.5% and 57.9% was found at 30-s for PPDI and TDI, respectively.

Figure IV.7. The time-dependent fluorescence intensity of **P2** film (2-3 nm) upon exposure to TDI vapor (room temperature) at 0, 10, 20, 30, 40, 50, 60, 90, 120, 180 and 240s (top to bottom). Inset: the FRQ (%) as a function of time

Figure IV.8. The time-dependent fluorescence intensity of **P2** film (2-3 nm) upon exposure to PPDI vapor (room temperature) at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 120s (top to bottom). Inset: FRQ (%) as a function of time

Table IV.4. FQR to isocyanates (**P2** film in 2-3 nm thickness) at 5 minutes

	PPDI	TDI	NDI	CPI	PI	MDI	IPDI
FQR (%)	84.0	76.1	28.7	19.1	17.3	5.1	-

Table IV.4 shows the FQR of polymer **P2** to vapors of seven isocyanates with exposure time of one minute. In general, the FQR follows the similar trend as for polymer **P1**. The FQR to PPDI (84%) and TDI (76.1%) is much larger than the one to NDI (28.7%) at the first minute. The difference for NDI is partly due to the relatively low vapor concentration (or molarity of NCO groups) of NDI. From the data in Table IV.1, vapor concentration of TDI is about 10 times of NDI and vapor concentration of PPDI is 5-6 times of NDI, which means much fewer NDI molecules could be adsorbed on the surface and trapped in the film. In addition, the size of these compounds could also play a role, as PPDI and TDI are smaller than NDI and may better fit into the polymer cavity.

Figure IV.9. FQR to vapors of PPDI, TDI and NDI at 60-s exposure, each pair are done by 2 nm and 33 nm **P2** films, respectively.

The study of thickness effect was done using films with thickness of ca. 2 nm and 33 nm that were exposed to vapors of PPDI, TDI and NDI for 1 minute (Figure IV.9). Clearly, the thinner film gives much larger FQR and the fluorescence intensity decreased greatly for the analytes of PPDI and TDI.

Detection of PPDI, TDI and NDI was further done using **P2** films in an optimal thickness of 2-3 nm over a longer period of time. The FQR at 10, 30, 60 and 120s exposure are summarized in Tables IV.5. Upon exposure of these three isocyanate vapors at 10s, PPDI lead to the strongest PL quenching (FQR: 45.2%), and TDI quenched more than NDI (FQR: 10.3%). The same trend is observed for all the other time periods. PPDI lead to rapid and large fluorescence drop and more than 90% of fluorescent intensity is decreased after 120-s exposure to PPDI vapor. And for TDI, there is over 80% reduced after 120-s exposure.

Table IV.5. FQR of films (2-3 nm) of **P2** to vapors of PPDI, TDI and NDI at given times

PPDI			TDI		NDI	
FQR (%)	10s	45.16	10s	23.90	10s	10.25
	30s	71.48	30s	57.90	30s	16.90
	60s	84.01	60s	76.10	60s	28.71
	120s	91.51	120s	84.93	120s	45.03

IV.5 Conclusion

The method based on the fluorescence quenching mechanism is first used to detect vapor of isocyanate compounds. Study on the thickness effect indicates that the thinner film (2-3 nm) gives a better result in terms of faster and larger PL quenching. Comparing

these two polymers for isocyanate detection, both of fluorescent intensity decreased after exposure to isocyanate vapor at a given time and good selectivity is shown towards different isocyanates. Under the same time of exposure and in the film of similar thickness, **P2** shows much larger response than **P1**, especially for PPDI, TDI and NDI. Both polymer **P1** and **P2** films show poor response to aliphatic isocyanate (IPDI). Considering the synthetic routes, costs and sensing performance, polymer **P2** is a good candidate for isocyanate sensing and for further application in optic-fiber sensors.

IV.6 Experimental Section

Calculations of vapor concentrations (D_2) and molarity of NCO groups (D_3)

D_1 (original vapor pressure by converted unit): 1 mmHg = 0.133 kPa;

D_2 (vapor concentration in the unit of pg/mL):

$$PV = nRT, P/RT = n/V,$$

$$M \cdot (P/RT) = (n/V) \cdot M = g/L,$$

$$\frac{P \cdot M}{8314 \times 293} = \frac{g}{L} = \frac{10^{12} \text{ pg}}{10^6 \text{ mL}}$$

$$D \text{ (pg/mL)} = D \text{ (g/L)} \times 10^6 = PM/RT \times 10^6$$

Where, P is x Pa, R is 8314 Pa L/mol K.

For example, D_2 of TDI:

$$D_2 = 1.33 \times 174.16 / (8314 \times 293) \times 10^6 = 95.09 \text{ pg/mL}$$

D_3 (the molarity of NCO groups in the isocyanate vapor):

$$PV = nRT, \text{ and } P/RT = n/V \text{ (mol/L) and } 1 \text{ mol/L} = 10^6 \text{ mol/L}$$

Setup and procedure for isocyanate detection

The setup and measurement of the changes in fluorescence intensity is almost the same as DNT sensing study. The only difference is that the isocyanate samples are always kept in the fume hood throughout the detection due to the high toxicity of isocyanate compounds. Some target isocyanates are solid at room temperature, and some are liquid. For solid isocyanates, about 50 mg of each compound was put in the bottom of a 20 mL vial with gauze on top, respectively. For liquid isocyanates, only several drops of each one were placed in 20 mL vial. The sample was stored no longer than 2 days in desiccators at ambient temperature.

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APPENDIX A

^1H and ^{13}C NMR Spectra and Assignments of Compounds 3-6

1D proton

Figure A.1. ^1H NMR (300 MHz, CDCl_3) spectra of compound 3

1D proton

Figure A.2. ^1H NMR (300 MHz, CDCl_3) spectra of compound 4

Table A.1. ^1H and ^{13}C NMR assignments of compounds 3-6

Compounds	^1H NMR	δ , ppm	Compounds	^{13}C NMR	δ , ppm
<p>3</p>	H1 H2 H3 H4	6.60 5.80 7.43 7.04	<p>3</p>	C1 C2 C3 C4 C5 C6 C7	135.36 183.48 151.90 47.36 143.57 124.40 125.56
<p>4</p>	H1 H2 H3	6.97 7.36 5.77	<p>4</p>	C1 C2 C3 C4 C5 C6	125.46 124.24 143.65 47.39 150.95 179.96
<p>6</p>	H1 H2 H3 H4 H5	6.96 7.36 5.80 3.90 0.51	<p>6</p>	C1 C2 C3 C4 C5 C6 C7 C8 C9	125.2 123.8 144.9 52.2 114.8 144.1 100.7 102.5 0.31

APPENDIX B

^1H and ^{13}C NMR Spectra and Assignments of Compound 9

Figure B.1. ^1H NMR (300 MHz, DMSO-d_6) spectrum of compound **9**

Figure B.2. ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of compound **9**

Table B.1. ^1H and ^{13}C NMR assignments of compound **9**

Compound	^1H NMR	δ , ppm	Compound	^{13}C NMR	δ , ppm
<p>9</p>	H1 H2	8.50 11.00	<p>9</p>	C1 C2 C3 C4	121.6 139.2 135.9 169.3