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

By

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ABSTRACT

The overall objectives of this thesis are (i) to design, synthesize and characterize new fluorescent polymers for explosive sensing applications, (ii) to study sensing properties of these polymers towards DNT using standard lab-equipments and fiber-optic probe, (iii) to correlate the structural features to the sensing performance.

Two new series of conjugated polymers having the fluorene and diphenylamine units in the polymer backbone and methyl ester, benzoyl, hydroxydiphenylmethyl, and cholesterol ester as the pendent groups were successfully synthesized through the Suzuki cross-coupling reaction, based on a design concept of simple structure, easy synthesis and large pendent groups to impart large free volume to the polymers for better sensing. The polymers and their monomers were fully characterized by NMR and IR spectroscopy. Glass transition temperatures of polymers ranged from 91 to 224 °C, while the onset temperatures for 5 % weight loss ranged from 291 to 441 °C. Absorption and photoluminescence of the diphenylamine series (**II-4, 6, 8, 10**) are red shifted due to the donor-acceptor interaction in comparison with the fluorene-based series (**II-5, 7, 9, 11**). The latter series have much higher fluorescence quantum efficiencies (e.g., 0.61).

Both the pendent groups and the units in the main chain can affect or contribute to the free volume of the polymers, which in turn affect the sensing performance. The polymers with large pendent groups and rigid bulky backbone show excellent fluorescence quenching efficiency, being equal or better explosive sensing performance than the best reported polymers to date. Considering the synthetic routes, costs and

sensing performance, polymers **II-5** and **II-11** are the best candidates among all the synthesized polymers for TNT sensing and for further application in fibre-optic sensors.

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CHAPTER I

Introduction to Conjugated Polymer-based Explosive Sensors

I.1 Background and Motivation

With the rising of global terrorism threats and the increased use of explosives in terrorist attacks, law enforcement agencies around the world are faced with the problem of detecting hidden bombs in luggage, courier packages, vehicles, on suspected individuals, and aircrafts¹. There are also significant concerns on the global landmine problem. The presence of landmines in countries recovering from war makes it extremely costly and difficult to carry out reconstruction and provide aid relief. The problem of unmarked minefields also deprives poor communities of land and infrastructure. According to the United Nations, there are approximately 110 million unexploded landmines, most of them are unmarked, and buried in more than 80 countries². Another worldwide problem involving on-site environmental detection and monitoring of traces of explosives and their degradation products is necessary in areas suspected of being contaminated by toxic explosives in order to monitor the quality of ground groundwater and prevent poisoning the nearby populations of humans and animals³. The development of efficient and cost-effective landmine detection devices has become an urgent world necessity.

Metal detectors are commonly used as an indirect technique for sensing explosive devices packaged in metal. This method is valuable for certain applications, such as landmine and weapon detection, but many modern landmines are packaged in plastic casings⁴. Because canines have excellent smell-detection capabilities, they are considered the most reliable tool for the detection of explosive vapors; however, there are several problems associated with using dogs to detect explosives⁵. They require rigorous training, testing and validation exercises in various operational scenarios with variety of

explosives and this has proven to be a costly method⁶. The dog's performance frequently declines over time and after extensive fieldwork, they are easily fatigued and require care. This has become a major analytical problem, which requires highly sensitive, specific and fast methods for its solution.

There are varieties of methods for explosive detection such as ion mobility spectrometry, gas chromatography coupled with mass spectrometry⁷, surface enhanced Raman spectroscopy⁸, energy dispersive X-ray diffraction⁹, cyclic voltammetry¹⁰, and electron capture detection³ currently available. Even though these methods are highly precise and sensitive, the instrument and equipments are either too large, expensive, need to be calibrated frequently, or too sophisticated to handle that are not easily applied to on-field testing.

I.2 Types of Explosives

An explosive material is made of energetically unstable chemical compounds that can be initiated to undergo a very rapid and self propagating decomposition, producing sudden expansion in volume that are usually accompanied by the production of heat and sudden pressure effect.

Based on the chemical structures and the performance and rates of decomposition, explosives are classified into several types (Figure I.1). Explosives are typically classified as low and high explosives and both types are further divided into a few sub-categories. Low explosives are propellants that burn rapidly (or deflagrate) at a rate of (cm s^{-1}). Low explosives are usually mixtures of combustible substances and an oxidant that decomposes rapidly; included in this group are propellants, smokeless powder, black

power, pyrotechnics and illumination devices such as flares¹¹. Unlike low explosives, high explosives undergo chemical reaction detonation at velocities of km s^{-1} exceeding the velocity of sound. High explosives are conventionally subdivided into two classes differentiated by sensitivity, primary and secondary explosives. Primary explosives, including lead azide and lead styphnate, are extremely sensitive to mechanical shock, friction, and heat to which they are highly susceptible to initiation and are often referred as ‘initiating explosives’ because they can be used to ignite secondary explosives. Secondary explosives also called base explosives which include nitroaromatic and nitramines, are relatively insensitive to shock, friction, and heat and thus are more suitable for use at military and industrial sites than primary explosives. Secondary explosives are often used as main charge or bolstering explosives because they are programmed to detonate only under specific circumstances.

Figure I.1. Classification of explosives based on structure, performance and sensitivity (Adopted from Ref.11).

Generally speaking, secondary explosives are mixtures of high explosives commonly based on nitroaromatics such as trinitrotoluene (TNT). TNT, an inexpensive compound, is a component found in fifteen explosive compositions. For instance, TNT is widely used in industrial explosives containing ammonium nitrate. Tritonal is a mixture of TNT and Al powder, and Amatol contains ammonium nitrate and TNT. Pentolite is a mixture of pentaerythritoltetranitrate (PETN) and TNT, and Composition B is a blend of cyclotrimethylenetrinitramine (RDX) and TNT⁴. Because of widespread use and volatility, nitroaromatics are an important general class of explosives for various detections¹². Chemical structures of some nitroaromatic explosives are shown in Figure I.2.

Figure I.2. Structures of some common nitroaromatic, nitramine, and nitrate explosives.

Interference is a major problem concerning soil sampling for the detection of unexploded landmines. Because landmines are buried beneath a layer of earth, trace detection is often limited to collecting vapour samples over the surface of the soil. This

narrows the focus to the more volatile explosive components, such as and dinitrotoluene (DNT) and TNT, whose equilibrium vapour pressures are roughly 100 and 5 ppb, respectively¹³. DNT is present in TNT samples as an impurity resulting from the manufacturing process. Even though there is only a small amount present, the significantly higher vapour pressure of DNT often makes it the target molecule for detection¹².

I.3 Conjugated Polymers for Explosive Detection

In 1977, Heeger and McDarmid and Shirakawa discovered that polyacetylene (molecular wire concept) can be doped to form new class of conducting polymers in which electrical conductivity can be systematically controlled over the full range from insulator to semiconductor to metal¹⁴. Polyacetylene has a linear, extended, π -conjugated structure, in which each carbon is σ bonded to single hydrogen and two neighbouring carbon atoms consistent with sp^2 hybridization. The π electrons are therefore available to delocalize into a band. In the ideal situation of a uniform chain, the resulting conduction band would give rise to metallic behaviour. The system itself is unstable with respect to bond alternation, which causes the formation of an energy gap in the electronic spectrum. Studies of π - π^* transitions in short-chain polyenes show that the frequencies do not fall as n^{-2} as expected for a free-electron, but appear to saturate at $\Delta E_{(n \text{ large})}^{\pi-\pi^*} \approx 2.4 \text{ eV}$. The bond alternation present in polymer is an important attribute leading to semiconducting behaviour¹⁴.

Further studies led to understanding and synthesis of conjugated (conducting) polymers that allow for the design and synthesis of molecular wires with tailored properties. In 1995, Swager and coworkers investigated molecular-based sensory

materials in which synthetic receptors are connected directly to a conjugated polymer backbone¹⁵. Using this approach, the fluorescent explosive-receptors are “wired in series”, which greatly enhance fluorescence-based chemosensory response of the polymers relative to single receptor sensory molecules.

Most nitroaromatic explosives can be exploited in the fluorescence-quenching detection scheme due to their electron accepting capability. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty π^* orbital, thus making these compounds good electron acceptors. As a result, reduction potentials become more favourable (less negative) as nitro substitution increases, according to nitrobenzene (-1.15 V), DNT (-0.9 V), and TNT (-0.7 V)¹⁶. 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 phase¹⁷. The interaction between the conjugated polymer and the explosive analyte is often achieved through an electron-transfer donor-acceptor mechanism, as depicted in Figure I.3. Electron deficient analytes, such as nitroaromatics, can act as electron acceptors for photo-excited electrons of the polymers.

Figure I.3. Electron-transfer fluorescent quenching (Adopted from Ref. 12).

Conventional fluorescence detection normally measures an increase or decrease in fluorescence intensity of an emission wavelength shift that occurs when a single molecule of the analyte interacts with an isolated chromophore. In that particular case, only the chromophore that interacts directly with the analyte molecule is quenched; the remaining chromophore molecules continue to fluoresce (Figure I.4a). A variation of this approach is the “molecular wire” configuration, in which the absorption of a single photon of light by any chromophore will result in a chain reaction, quenching the fluorescence of many chromophores and amplifying the sensory response by several magnitudes (Figure I.4b)¹⁸.

Figure I.4. Polymer amplification mechanism. (a) Traditional chemosensor. (b) Receptors wired in series. Green is the emissive polymer, blue the quenched, and red is the analyte; $h\nu$ is the light at the excitation wavelength, $h\nu'$ at the emission wavelength. (Adopted from Ref. 18)

I.4 Electron-Transfer “Turn-on/Turn-off” Mechanism

The alternative method to the fluorescent quenching detection is to remove quenching sites by interactions with an analyte and create an increase in fluorescence, the so called “turn-on” response. Photoinduced electron transfer (PET) sensors are an important family of chemosensors and molecular fluorescence turn-on sensors have been studied on the basis of PET mechanism. In such a system, the receptors usually contain a relatively high energy non-bonding electron pair. In absence of analytes, this electron pair quenches the fluorescence of the chromophore by rapid intramolecular electron transfer from the receptor to the excited chromophore. When this electron pair is coordinated to

Lewis acid cations, the HOMO of the receptor is lowered. This decreases the driving force for the PET process and can turn on the fluorescence of the chromophore¹⁹.

To accommodate the intramolecular electron transfer, the inter-quencher spacing is usually less than the exciton diffusion length. In this case, the sensitivity of the turn-on response will decrease in comparison with the case of the turn-off method. More specifically, removing a quenching site may not give a desired response because another quencher's influence could overlap much of the same quenching volume. Turn-on signal (increase in fluorescence) is not always easier to detect than a quenching signal. Turn-on signal is only observed, provided that there is no fluctuation in the background noise of the fluorescence detection electronics and the background is completely dark. However, when there is background fluorescence, which often is the case, there is no added advantage of the turn-on over turn-off response.

Figure I.5 shows the dimensionality and quenching mechanism as they relate to the sensitivity of an amplified fluorescent polymer-based sensor. The horizontal direction illustrates that the quenching (or unquenching) of polymer chains in solution is less sensitive than that in thin film. Vertical axis shows the unquenching (turn-on) is generally less sensitive than quenching because many quenchers may have to be removed in order to observe a signal enhancement. It is also possible that quencher can also be emissive and thereby function as a turn-on sensor. Unquenching generally results in overlapping quenching domains and is less sensitive than quenching. Sensitivity increases as polymer chains are assembled into structures that provide the exciton with additional energy migration pathways that exhibit greater efficiency. In the case of sensors for ultra-trace

detection, a quenching mechanism with the highest level of dimensionality for exciton diffusion is preferred²⁰.

Figure I.5. Mechanism, dimensionality and relative sensitivities of turn-on and turn-off sensors. (Adopted from Ref. 20)

I.5 Fiber-optic Probe

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 effectiveness of the fluorescent quenching method. A thicker film can generate a higher emission level due to the unquenched underlayer that does not interact with explosive vapours, thus 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 excited sites has become critical for ultra-trace sensing. Although the level of fluorescent signal is directly

proportional to the level of excitation power, this is only true for lower-level illumination. With a high excitation power, the polymer tends to degrade or is permanently damaged. Strong excitation can cause continuous drop in signal level, which could produce false quenching effect. These problems may arise from using conventional high-performance lab-based equipment such as a spectrophotometer or fluorimeter. Lab-based equipments are simply not practical for a portable, cost-effective system capable of remotely accessing hard-to-reach areas, which is highly desired for explosive detection.

A possible solution to these problems is fiber-optic sensing. Optic fibers are low-cost, flexible and lightweight, with extremely low loss over long transmission distances. With a proper setup, a fiber-optic 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 with a 400 μm core for spectral display and analysis. The light source can be an argon laser or light-emitting diode. The fiber-optic fluorescent sensor can reduce stray excitation light and signal fluctuation, enhance signal stability, and provide up to 2.5 times more sensitive sensing capability over the conventional laboratory equipment.

I.6 Design Rationale and Objectives

Good electron acceptors can efficiently quench fluorescence by photoinduced electron transfer. In 1998, Swager used fluorescence quenching transduction mechanism together with the amplifying nature of conjugated polymers to design a pentiptycene containing polymer (Figure I.6). This material is highly sensitive to TNT or DNT vapour, showing rapid quenching of its blue luminescence (465 nm) at sub-part-per-trillion (ppt)

levels of analytes^{21,22}. The long conjugated polymer chain provides exciton delocalization along the chain, which contributes to the exceptional sensitivity. Another important design is the use of the rigid pentiptycene group, which prevents interchain π stacking and self-quenching of luminescence and also makes the polymer have a large free volume for trapping analyte molecules.

Figure I.6. Pentiptycene containing polymer, poly(*p*-phenylene-ethynylene).

Aside from preventing polymer chain interactions, the bulky pendent groups also contribute to a greater photochemical stability of thin films. Fluorescence intensity does not change significantly with heating or solvent washings. The porous structure in polymer film is critical for successful ultra-trace detection because it permits quenchers to penetrate rapidly and deeper into the film.

Amplification also depends on how many binding sites each exciton can visit. The potential way to improve this quantity is to increase the fluorescence lifetime of the sensing material. If each exciton has a longer time before it decays intrinsically to ground state, exciton may be able to sample more locations within the polymer film. Fused polycyclic aromatics often have forbidden or weakly allowed transition that can result in a longer excited-state lifetime²³.

To further advance the study of chemical sensors for the rapid detection of explosives, in this thesis work we have designed two series of fluorescence “turn-off” polymers (**I** and **II**, Scheme I.1) for the detection of explosive materials, e.g., 2,4,6-trinitrotoluene (TNT) or 2,4-dinitrotoluene (DNT). The design is based on two structural criteria: conjugation in polymer backbone and large pendent groups. The phenylene backbone in polymer **I** is expected to be better delocalized than the amino phenylene backbone in polymer **II**, thus being more fluorescent. The three side groups, methyl ester, benzoyl and large cholesterol ester, are to be used, which are different in size or have different site-isolation effect and thus can be compared for the fluorescence quantum yields and sensing efficiency of the corresponding polymers. In addition, the keto group (or benzophenone moiety) is expected to lower the fluorescence quantum yield of the corresponding polymers, in comparison with the ester. Finally, the reason to choose the diphenylamine unit in polymer **II** is to probe if there is any preferred donor-acceptor interaction between the diphenylamine moiety and the nitroaromatic molecule, which may enhance the detection sensitivity.

Scheme I.1. Design and retrosynthetic analysis of conjugated polymers for explosive sensing.

The target polymers are designed with consideration of structural simplicity and ease in synthesis. These polymers can typically be synthesized by condensation of two monomers via Suzuki-coupling reaction. As shown by retrosynthetic analysis in Scheme I.1, the two series of polymers share one same dibromo monomer, and another monomer, fluorene diboronic acid or ester, is commercially available. The diphenylamine-containing monomer can be synthesized according to the known methods in literature. The alkyl group (R') is typically eight or ten carbon aliphatic chain, which can impart the solubility to the polymers. By cross-coupling each of three dibromo monomers with two diboronic monomers, there are a total of six polymers to be synthesized and thus available for explosive sensing tests and probing the structure-property relationships.

Therefore, the overall objectives of this thesis work are:

- (1) to synthesize and characterize two new series of simple fluorescent polymers having fluorene and diphenylamine units in polymer backbone,
- (2) to study sensing properties of these polymers towards DNT using standard lab fluorimeter and fiber-optic probe, and
- (3) to correlate the structural features to the sensing performance of the polymers.

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CHAPTER 2

Synthesis and Characterization of Monomers and Polymers

II.1 Overview of Suzuki Cross-Coupling Reaction

Palladium-catalyzed cross-coupling of organoboronic acids with aryl chlorides, bromides, iodides, or triflates, known as the Suzuki reaction, is among the most powerful and versatile synthetic methods for carbon-carbon bond formation. The reaction has a broad scope and is highlighted by its tolerance of a wide range of functionality and the use of water as a solvent. Since a variety of organoboron derivatives are now commercially and synthetically available, stable in the air and inert to various functional groups, a number of studies on transition-metal-catalyzed cross-coupling reactions of organoboronic acids or esters have been reported.

Organoboron compounds are highly electrophilic, but the organic groups on boron are weakly nucleophilic, thus limiting the use of organoboron reagents for the ionic reactions. The coordination of a negatively charged base on the boron atom has been recognized to be an efficient method of increasing its nucleophilicity to transfer the organic group on boron to the adjacent positive center (1, 2-migration reaction)¹⁻³.

The catalytic cycle for the cross-coupling reaction of organometallics involves mainly three sequences: oxidative addition-transmetallation-reductive elimination (Figure II.1). Although each step involves further processes including ligand exchanges, it is significant that the great majority of cross-coupling reactions catalyzed by Ni(0), Pd(0), and Fe(I) are rationalized in terms of this common catalytic cycle.

Figure II.1. A general catalytic cycle for Suzuki cross-coupling.

Oxidative addition of halide compounds to a palladium(0) complex affords a stable *trans*- σ -palladium(II) complex and is often the rate-determining step in a catalytic cycle. It is called oxidative addition because the formal oxidation state of the transition metal changes from $\text{M}(0)$ to $\text{M}(\text{II})$ in the process⁴. The reactivity decreases in the order of $\text{I} > \text{Br} \gg \text{Cl}$. Aryl halides activated by the proximity of electron-withdrawing groups are more reactive to the oxidative addition than those with electron-donating groups, thus allowing for the use of chlorides in the cross-coupling reaction. A very wide range of palladium(0) catalysts or precursors can be used for cross-coupling reaction. $\text{Pd}(\text{PPh}_3)_4$ is most commonly used, but $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{OAc})_2$ plus PPh_3 or other phosphine ligands are also efficient since they are stable to air and readily reduced to active $\text{Pd}(0)$ complexes with organometallics or phosphines used for the cross-coupling⁵⁻⁹.

The palladium(II) intermediate generated in the oxidative addition step then undergoes transmetallation with the boron compound. The nucleophile (R^1) is transferred from the metal in the organometallic reagent to the palladium(II) complex, followed by reductive elimination to give the coupled product (R^1-R^2) and the palladium(0) catalyst ready for another cycle.

II.2 Synthesis of Polymers II-4 and II-5

The synthetic route toward dimethyl 2,5-dibromoterephthalate (**II-1**) is outlined in Scheme II.1. Compound **II-1** was prepared in three steps, starting from commercially available *p*-xylene with excess bromine at room temperature for approximately one day with a small amount of iodine as a catalyst. 1,4-Dibromo-2,5-dimethylbenzene was oxidized using potassium permanganate in aqueous pyridine followed by esterification with methanol to give **II-1** with a yield of 90 %.

Scheme II.1. Synthesis of dimethyl 2,5-dibromoterephthalate (**II-1**).

The bromination of *p*-xylene occurs at the 2,5-positions because alkyl groups specifically direct electrophilic substitution at the *ortho* and *para* positions. There is small inductive effect between any sp^2 and sp^3 carbon atoms, if this were the only effect, then the carbon to which the alkyl group is attached (the *ipso* carbon) should have the greatest electron density¹⁰, followed by the *ortho* carbons, then the meta carbons, and finally the

carbon atom furthest from the substituent, in the *para* position. The proposed mechanism for bromination reaction is shown below;

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 no matter what their length. In order for the reaction to proceed, there must be at least one hydrogen in the benzylic position¹¹. The details are vague but the reaction is believed to involve the formation of MnO_4^- ions that is Mn(VII), from manganate ion in aqueous solution. Under the basic condition, these form the “manganate esters” with alcohols. The esters decompose by elimination of HMnO_3 to yield the carboxylic acid group in the final product.

In esterification of RCO_2H , the carbonyl group may be protonated first by acid. Only strong acids are powerful enough to protonate carbonyl groups (i.e. HCl and H_2SO_4), however weaker acids are still sufficient to increase the rate of substitution reactions at carbonyl groups, because those carbonyl groups become extremely powerful electrophiles once being protonated. It is for this reason that alcohols will react with carboxylic acids with an acid catalyst.

The Suzuki cross-coupling reactions of compound **II-1** with N-hexyl-4,4'-dibromodiphenylamine and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) afforded polymers **II-4** and **II-5**, respectively (Scheme II.2). It should be mentioned that the polymerization did not proceed with 2,5-dibromoterephthalic acid and the esterification step was necessary.

Scheme II.2. Synthesis of polymers **II-4** and **II-5** by Suzuki cross-coupling reaction.

II.3 Synthesis of Polymers **II-6** and **II-7**

Attempts were made to synthesize compound **II-2** as another dibromide monomer from the ester precursor **II-1** using the Grignard and organolithium reagents. The

Grignard reagent (PhMgBr) was synthesized by oxidative insertion or oxidative addition of magnesium into the carbon-halogen bond in bromobenzene. Subsequent addition of dimethyl 2,5-dibromoterephthalate might only have triggered transmetallation reaction rather than nucleophilic reaction at the ester group. As a result, no nucleophile attack occurred at the C=O bond and the reaction did not happen. The compound was isolated and analyzed by ^1H and ^{13}C NMR and no trace of Br in the product was found by mass spectrometry. To prevent the transmetallation process occurring between the Grignard reagent and aryl bromide, polymers **II-4** and **II-5** were used instead. No reaction was observed, as IR analysis of the isolated polymers still showed the ester groups.

n-Butyllithium was then used on compound **II-1**. However, the outcome was similar to that of the Grignard reagent and thus the reaction was unsuccessful. The failure may have arise from the weak electrophile of the ester's C=O site and partially from the high sensitive nature of organolithium reagent.

Scheme II.3. Synthesis of 2,5-dibromo-1,4-dibenzobenzene (**II-2**).

To remediate the reaction condition, an entirely new approach was conceived (Scheme II.3). Not all carbonyl derivatives are equally reactive, the hierarchy of reactivity is as follows:

The reactive hierarchy 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: good nucleophiles are bad leaving groups, thus poor reactivity¹². With the reactivity in mind, we considered converting 2,5-dibromoterephthalic acid into an acid chloride followed by Fridel-Crafts acylation to afford compound **II-2**. Acylation is a powerful method because it does not require any particular structural feature in the acyl chloride --- R can be almost anything. The reaction mechanism is shown below.

Thionyl chloride reacts with the OH group of a carboxylic acid turning it into a good leaving group, producing acyl chloride intermediate. Fridel-Craft acylation of acid chloride give compound **II-2**.

Suzuki cross-coupling reaction between compound **II-2** with N-hexyl-4,4'-dibromodiphenylamine and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) gave polymers **II-6** and **II-7** (Figure II.2).

Figure II.2. Structures of polymers **II-6** and **II-7**.

II.4 Synthesis of Polymers **II-8** and **II-9**

Further reacting polymers **II-6** and **II-7** with excess organolithium reagent afforded two new polymers **II-8** and **II-9** containing the bulky pendent groups (Figure II.3). Phenyllithium was added to the dissolved polymer in THF at -78°C . After stirring at room temperature overnight, the reaction was quenched with aqueous NH_4Cl , and subsequent workup gave polymers **II-8** and **II-9**.

Figure II.3. Structures of polymers **II-8** and **II-9**.

II.5 Synthesis of Polymers II-10 and II-11

A new monomer **II-3**, an analog to monomer **II-1**, is the next desirable target, as its large ester groups may impart more free volume or void in the resulting polymers, beneficial for explosive sensing. Monomer **II-3** was made in two steps, starting from 2,5-dibromoterephthalic acid (Scheme II.4).

Scheme II.4. Synthesis of 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 (**II-3**).

It is expected that an acid chloride to be particularly good at $\text{S}_{\text{N}}2$ reactions as chloride ion is a very good leaving group. The added tetraalkylammonium salt is a phase transfer catalyst that has a polar group (N^+) and hydrocarbon side chains. These long chains keep the $\text{BnEt}_3\text{N}^+\text{RO}^-$ ion pairs being soluble in organic phase during the reaction. The ammonium salt also acts as a base catalyst for the reaction and the proposed mechanism is as follows.

The Suzuki cross-coupling reactions between monomer **II-3** with N-hexyl-4,4'-dibromodiphenylamine and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate), respectively, afforded polymers **II-6** and **II-7** (Figure II.4).

Figure II.4. Structures of polymers **II-10** and **II-11**.

II.6 Characterization of Monomers and Polymers

The obtained monomers and polymers are completely soluble in common organic solvents, such as toluene, THF, and chloroform. The inherent viscosity of these polymers was determined using Ubbelohde viscometer (size OB114) in 0.5 % (g/dL) chloroform solution at 30 °C. Characterization of all the intermediates, monomers and polymers were performed using infrared (IR), nuclear magnetic resonance (NMR) and mass spectrometry. Decomposition temperatures of polymers were measured by

Thermogravimetric Analyzer (TGA), and glass transition temperatures of polymers were measured by Differential Scanning Calorimetry (DSC).

II.6.1 Infrared Spectroscopy

The IR analysis was done with thin films of polymers, which were cast on the NaCl salt plates. As for the characterization of polymers, polymers **II-4** and **II-5** containing pendent ester groups exhibit intense C=O band in the range of 1731-1734 cm^{-1} (lit.¹³ 1715-1740 cm^{-1}), slightly shifted due to the conjugation with the phenyl moiety. Polymers **II-6** and **II-7** containing the pendent keto groups show a strong band for the C=O group at 1664-1668 cm^{-1} . This band is also shifted to a lower frequency due to the conjugation.

The IR spectra of polymers **II-8** and **II-9** show a strong band in the range of 3529-3548 cm^{-1} , characteristic of alcohol functional groups. Polymers **II-10** and **II-11** containing esters moieties display strong band at 1716-1726 cm^{-1} , which is also affected by the conjugation of phenyl group. Characteristic peaks of polymers **II-4** to **II-11** are summarized in Table II.1.

Table II.1. Characteristic IR peaks of polymers **II-4** to **II-11**.

Polymer	Characteristic IR peaks (cm⁻¹)
II-4	3031-2856 (C-H sp ² aromatic and sp ³ aliphatic) 1731 (C=O ester), 1601 (C=C)
II-5	2936-2867 (C-H sp ² aromatic and sp ³ aliphatic) 1734 (C=O ester), 1663 (C=C)
II-6	3031-2856 (C-H sp ² aromatic and sp ³ aliphatic) 1664 (C=O ketone), 1598 (C=C)
II-7	3060-2854 (C-H sp ² aromatic and sp ³ aliphatic) 1668 (C=O ketone), 1596 (C=C)
II-8	3529 (OH) 3059-2856 (C-H sp ² aromatic and sp ³ aliphatic) 1600 (C=C)
II-9	3548 (OH) 3061-2855 (C-H sp ² aromatic and sp ³ aliphatic) 1599, 1461 (C=C)
II-10	3010-2867 (C-H sp ² aromatic and sp ³ aliphatic) 1716 (C=O ester), 1600 (C=C)
II-11	2930-2853 (C-H sp ² aromatic and sp ³ aliphatic) 1726 (C=O ester), 1464 (C=C)

Infrared spectroscopy was the best method to identify polymers **II-8** and **II-9** derived from polymers **II-6** and **II-7**. Due to the structural differences (ketone and tert-alcohol) between the two polymer series, reaction progress was monitored by simply analyzing the IR spectra that were taken at various time intervals throughout the entire length of the reaction.

II.6.2 NMR Spectroscopy

NMR analyses were done for all the monomers (**II-1** to **II-3**) including all the synthetic intermediates. ¹H and ¹³C assignments were done with the aid of COSY and HETCOR experiments. For compound **II-3**, because of major overlapping in the aliphatic

regions, only the peaks that are vital for the identification of the compounds were assigned. The ^1H and ^{13}C NMR data are reported in Table II.2. The spectra, Figure A.1 to A.8, are in the appendix.

Similarly, polymers **II-4** to **II-11** were also characterized by ^1H and ^{13}C NMR using chloroform as a solvent (Tables II.2 to II.10). The peaks assignment of the monomers were particularly valuable in the assignment of the polymers especially the polymers containing cholesterol moieties. Due to the high overlapping of the alkane present in the molecular structures, only important peaks that are vital to the identification of their structures were assigned. To affectively identify the alcohol (OH) groups in polymers **II-8** and **II-9**, a drop of D_2O was added. The deuterium undergoes hydrogen exchange with the hydrogen atoms. As a result of deuterium exchange, the hydrogen peaks from the alcohol disappear from the ^1H NMR spectrum and produce instead a peak of DOH, this is an affective mean of identifying the OH groups present within the molecular structure of the polymers.

Table II.2. ^1H and ^{13}C NMR assignments of compounds II-1 to II-3

II-1		^1H NMR	δ , ppm	^{13}C NMR	δ , ppm
		H 1 H 2	3.96 8.06	C 1 C 2 C 3 C 4 C 5	52.9 164.5 136.6 120.2 135.4
II-2		^1H NMR	δ , ppm	^{13}C NMR	δ , ppm
		H 1 H 2 H 3 H 4	7.98 7.88 7.64 7.60	C 1 C 2 C 3 C 4 C 5 C 6 C 7	133.01 130.50 129.67 135.33 118.35 143.42 193.84
II-3		^1H NMR	δ , ppm	^{13}C NMR	δ , ppm
		H 1 H 2 H 3 H 4	8.00 4.92 2.52 5.49	C 1 C 2 C 3 C 4 C 5 C 6	76.47 19.36 11.87 18.73 22.58

Table II.3. ^1H NMR and ^{13}C NMR assignments of polymer II-4 (CDCl_3).

Polymer II-4	^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	3.8	H 5	7.13-7.16
	H 2	1.76	H 6	7.37-7.34
	H 3	1.53	H 7	7.85
	H 4	0.93-0.91	H 8	3.76
	^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	52.43	C 11	136.05
	C 2	26.79	C 12	140.17
	C 3	27.54	C 13	131.85
	C 4	31.83	C 14	168.81
	C 5	22.67	C 15	52.23
	C 6	14.04		
	C 7	129.35		
	C 8	120.56		
	C 9	147.36		
	C 10	131.85		

Table II.4. ^1H NMR and ^{13}C NMR assignments of polymer II-5 (CDCl_3).

Polymer II-5	^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	0.85-0.82	H 6	7.36
	H 2	1.15	H 7	7.85
	H 3	1.15	H 8	7.95
	H 4	2.19	H 9	3.69
	H 5	7.43
^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
	C 1	14.05	C 11	151.08
	C 2	22.58	C 12	119.86
	C 3	31.78	C 13	140.34
	C 4	29.37	C 14	139.04
	C 5	30.16	C 15	122.99
	C 6	30.92	C 16	127.23
	C 7	23.86	C 17	133.55
	C 8	40.63	C 18	141.29
	C 9	55.38	C 19	168.79
	C 10	52.15	C 20	131.83

Table II.5. ^1H NMR and ^{13}C NMR assignments of polymer II-6 (CDCl_3).

Polymer II-6	^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	7.68	H 6	7.20-7.17
	H 2	7.80-7.72	H 7	3.51
	H 3	7.34-7.28	H 8	1.45
	H 4	7.46-7.41	H 9	1.28-1.25
	H 5	6.62-6.59	H 10	0.91-0.87
^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
	C 1	52.00	C 11	129.93
	C 2	27.23	C 12	132.99
	C 3	26.63	C 13	140.42
	C 4	31.59	C 14	137.09
	C 5	22.63	C 15	139.13
	C 6	14.04	C 16	147.33
	C 7	198.62	C 17	131.65
	C 8	120.77		
	C 9	129.18		
	C 10	129.96		

Table II.6. ^1H NMR and ^{13}C NMR assignments of polymer **II-7** (CDCl_3)

Polymer II-7	^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	0.86-0.82	H 7	~7.60
	H 2	0.98	H 8	~7.67
	H 3	1.17	H 9	~7.57
	H 4	1.63	H 10	~7.37
	H 5	~7.32	H 11	~7.47
	H 6	~7.25
^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
	C 1	14.10	C 12	140.03
	C 2	22.45	C 13	139.78
	C 3	31.84	C 14	151.42
	C 4	29.01	C 15	127.93
	C 5	29.31	C 16	140.69
	C 6	30.19	C 17	136.42
	C 7	23.60	C 18	137.93
	C 8	40.21	C 19	198.46
	C 9	55.07	C 20	129.94
	C 10	120.00	C 21	128.83
	C 11	123.35	C 22	133.29

Table II.7. ^1H NMR and ^{13}C NMR assignments of polymer II-8 (CDCl_3)

Polymer II-8	^1H NMR	δ , ppm	^1H NMR	δ , ppm
	H 1	3.56		
	H 2	1.56		
	H 3	1.29		
	H 4	0.93-0.89		
	H 5	6.64-6.55		
	H 7	3.31		
			H 6, H 8, H 9, H 10, and H 11	7.27-7.25
	^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
	C 1	52.07	C 11	134.51
	C 2	27.23	C 12	138.42
	C 3	26.66	C 13	143.88
	C 4	31.27	C 14	147.45
	C 5	22.65	C 15	127.79
	C 6	14.07	C 16	128.04
	C 7	83.24	C 17	127.20
	C 8	119.99	C 18	146.57
	C 9	130.41		
	C 10	133.73		

Table II.8. ^1H NMR and ^{13}C NMR assignments of polymer II-9 (CDCl_3)

Polymer II-9	^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	0.87-0.83		
	H 2	1.02		
	H 3	1.20		
	H 4	1.56-1.51		
	H 9	3.15		
	H 5, H 6, H 7, H 8, H 10, H 11, H 12			7.25
^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
	C 1	14.14	C 12	140.75
	C 2	22.68	C 13	139.58
	C 3	31.92	C 14	135.21
	C 4	29.32	C 15	138.79
	C 5	29.47	C 16	143.33
	C 6	30.12	C 17	83.25
	C 7	23.90	C 18	138.79
	C 8	39.71	C 19	147.82
	C 9	55.01	C 20	127.79
	C 10	119.34	C 21	128.10
	C 11	123.81	C 22	127.25

Table II.9. ^1H NMR and ^{13}C NMR assignments of polymer **II-10** (CDCl_3)

Polymer II-10

^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	3.76	H 8	7.85
H 2	6.94-6.90		
H 3	7.35-7.32		
H 4	0.94-0.92		
H 5	4.70		
H 6	~2.23		
H 7	5.37		
		H 9, H 11, H 12, H 10	1.54-1.00

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	52.39	C 12	75.04
C 2	26.93	C 13	42.31
C 3	31.68	C 14	120.45
C 4	35.81	C 15	35.81
C 5	22.59	C 16	11.88
C 6	14.13	C 17	18.73
C 7	120.45	C 18	22.84
C 8	129.59		
C 9	147.32		
C 10	136.08		
C 11	167.99		

Table II.10. ^1H NMR and ^{13}C NMR assignments of polymer II-11 (CDCl_3)

Polymer II-11
^1H NMR	δ , ppm	^1H NMR
	H 1	0.87-0.82	H 9
	H 2	~1.03	H 10
	H 3	~1.36	H 11
	H 4	~1.51	
	H 5	~7.43	
	H 6	~7.43	
	H 7	~7.83	
	H 8	~7.85	
	H 12, H 13, H 14, H 15		~ 2.00-0.52
^{13}C NMR	δ , ppm	^{13}C NMR
	C 1	14.13	C 12
	C 2	22.68	C 13
	C 3	31.87	C 14
	C 4	29.58	C 15
	C 5	29.47	C 16
	C 6	30.12	C 17
	C 7	23.90	C 18
	C 8	39.70	C 19
	C 9	55.31	C 20
	C 10	119.62	C 21
	C 11	122.83	C 22

II.6.3 Inherent Viscosity

The molecular weight of a polymer is important in its synthesis and application. Thermal and mechanical properties 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.

Solution viscosity is used to estimate the molecular weight of a polymer. One of the most characteristic features of a dilute polymer solution is that its viscosity is considerably higher than that of a pure solvent¹⁴. This arises because of the large differences in size between polymer and solvent molecules. Generally when comparing polymers with similar structures, the higher the viscosity, the higher the molecular weight. The inherent viscosity values of polymers II-4 to II-11 were measured (Table II.11).

Table II.11. Inherent viscosities of polymers **II-4** to **II-11**.

N-hexyldiphenylamine basedPolymers	η_{inh} (dL/g) ^a	Fluorene-based Polymers	η_{inh} (dL/g) ^a
II-4 (ester moieties)	0.36	II-5 (ester moieties)	0.74
II-6 (ketone moieties)	0.11	II-7 (ketone moieties)	0.54
II-8 (tert-alcohol moieties)	0.29	II-9 (tert-alcohol moieties)	0.52
II-10 (cholesterol moieties)	0.25	II-11 (cholesterol moieties)	0.45

^a 0.5 g/dL in chloroform, measured at 30 °C.

The inherent viscosities for N-hexyldiphenylamine-based polymers range from 0.11 to 0.36 dL/g and the fluorene-based polymers range from 0.52 to 0.74 dL/g in chloroform. From the data, it is clear that N-hexyldiphenylamine-based polymers have low viscosities and thus lower in molecular weight than those of the fluorene-based

polymers. It is speculated that fluorene-based polymers have higher viscosities because of their rigid conjugated polymer backbone. It is also worth noting that as the size of the pendent groups increases, their inherent viscosities decreases; **II-5** > **II-7** > **II-9** > **II-11**.

II.6.4 Thermal Analysis

Since the conjugated polymers **II-4** to **II-11** are to be used in chemosensors, their thermal stability is one of major factors that needed to be determined. Thermogravimetric analysis (TGA) is a method in which the changes in the weight (mass) of a sample as a function of temperature and/or time can be measured and differential scanning calorimetry (DSC) measures the energy absorbed or released by a sample as a function of temperature or time. When thermal transition occurs in the sample, DSC provides a direct calorimetric measurement of the transition energy at the temperature of the transition. Therefore it can be an appropriate method to measure the glass transition temperature of the compounds in endothermic phase transition from a solid to rubbery state and the crystallization temperature of compounds when they undergo exothermic processes from liquid to solid.

Figure II.5. DSC traces (left) and TGA (right) of polymer **II-4**.

Polymers **II-4** to **II-11** were investigated by DSC) and TGA. The results are compiled in Table II.12. The T_g of all the polymers range from 91-224 °C. The decomposition temperatures (T_d), as assessed by the onset temperature of 5 % weight loss by TGA, occur in the range of 291-441 °C.

Table II.12. Thermal properties of polymers **II-4** to **II-11**

Polymers	Decomposition Temperature (T_d , °C) ^a	Glass transition Temperature (T_g , °C) ^b
II-4	413	97
II-5	435	91
II-6	415	115
II-7	441	94
II-8	292	224
II-9	404	94
II-10	291	100
II-11	312	155

^a By TGA for 5% weight loss in N₂ at a heating rate of 20 °C/min. ^b From third scan of DSC under N₂ at a heating rate of 10 °C/min.

All the N-hexyldiphenylamine-based polymers (**II-4**, **II-6**, **II-8**, and **II-10**) are amorphous. The polymers containing multiple phenyl moieties (e.g., **II-8**) possess slightly higher T_g when compared to their ester, ketone, and cholesterol counterparts. The decreased chain mobility due to bulky pendent groups can lead to an increase in glass-transition temperature. As is consistent with Naito's rationalization¹⁵, the glass-transition temperature is higher for a larger molecular structure: **II-8** > **II-10** > **II-6** > **II-4**. Similar trend was observed in fluorene-based polymers (**II-5**, **II-7**, **II-9**, and **II-11**).

The decomposition temperature (T_d) of polymers **II-4** to **II-11** is considered to be high, thus suitable for film preparation and device fabrication. Among all, the N-hexyldiphenylamine-based polymers (**II-4**, **II-6**, **II-8**, and **II-10**) displayed lower T_d

compared to their corresponding fluorene analogues due to the presence of alkyl-amino group which is less tolerant to high temperature. The decomposition temperature of polymers containing the cholesterol moieties (**II-10** and **II-11**) is also lower, due to the presence of long aliphatic groups.

II.7 Conclusion

Two new series of fluorescent polymers having fluorene and diphenylamine in the polymer backbone and the ester, ketone, tertiary alcohol, and cholesterol moieties as pendent groups were successfully synthesized. The general route to key monomers begins with readily available 2,5-dibromoterephthalic acid. All the polymers were fully characterized by infrared and NMR spectroscopy and by thermogravimetry and differential scanning calorimetry.

II.8 Experimental Section

II.8.1 Materials

Tetrahydrofuran (THF, Aldrich) was dried by refluxing over a bed of sodium and benzophenone. Other reagents and solvents were purchased at reagent grade 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 mm, 230-400 mesh) was used as the stationary phase for column chromatography.

II.8.2 Characterization

Infrared measurements were performed on a Varian 1000 FT-IR Scirnitars series. ^1H NMR and ^{13}C NMR were recorded in chloroform- d or DMSO- d on the Bruker Advanced Digital NMR 300 spectrophotometer and results are reported in ppm from tetramethylsilane on the δ scale. Decomposition temperatures of products were measured on a Thermogravimetric Analyzer (TGA) TGA 2950 CE Instrument at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. Glass transition temperature (T_g) of all the polymers were recorded by Differential Scanning Calorimetry (DSC) on DSC Q100 Instrument at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen (50 mL/min). For all DSC and T_g measurements, polymer pellets were lightly pressed, and a sample of 5-8 mg was used for each measurement. The T_g values were reported from the second scan. The T_g was taken from the midpoint of the change in the slope of the baseline. The UV absorptions of the compounds were recorded using a UV-vis Lambda 900 spectrophotometer while the photoluminescence of products were measured by Shimadzu RF-1501 spectrofluorophotometer, using 1 cm quartz cell. Inherent viscosity data were obtained with Ubbelohde viscometer (size OB114) in 0.5 % (g/dL) chloroform solution at 30 $^{\circ}\text{C}$.

II.8.3 Film Preparation by Casting and Spin Coating

Polymer films were cast from chloroform. Typically, a solution (5.0 mg in 1.0 mL of solvent) was transferred to a glass plate (microscope slides, length = 23 mm, width = 23 mm and thickness = 1.0 mm) and allowed to slowly evaporate at room temperature for 24 h. The thickness of the films ranged from 375 to 2930 nm.

The polymer solution (5.0 mg in 1.0 mL solvent) was transferred to a glass plate (microscope slide, length = 23 mm, width = 23 mm and thickness = 1 mm). Polymer films were spin-coated at 1000 rpm on the Chemat Technology Spin-Coater KW-4B. The layer thickness (approximately 65 nm) measurements of the polymer films were performed using a Tencor Instruments Alpha-Step 200 surface profiler.

II.8.4 Syntheses

*1,4-Dibromo-2,5-dimethylbenzene*¹⁶

Bromine (22.00 g, 140 mmol) was added dropwise into a stirred and ice-cooled solution of p-xylene (5.40 g, 50.0 mmol) and iodine (2-3 pieces). Light was rigorously excluded by wrapping the reaction flask with tin foil. After stirring at room temperature for 1 day, 20% KOH solution (5.00 g in 25 mL) was added and the aqueous layer was decanted. The residue was recrystallized from 95% ethanol (twice) to give white solids (7.90 g, 60%). ¹H NMR (300 MHz, CDCl₃) δ 7.41 (s, 2H), 2.35 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 136.9, 133.9, 123.3, and 22.11.

2, 5-Dibromoterephthalic acid

1,4-Dibromo-2,5-dimethylbenzene (3.00 g, 11.4 mmol) in pyridine (70 mL) and water (30 mL) containing 8.50 g of KMnO_4 was refluxed for 2 h. Every 30 min, 11 mL of water and 3.7 g of KMnO_4 were added. This was done 4 times. After 5-6 h, 74 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 pyridine and the aqueous layer was precipitated by adding concentrated HCl . The white precipitated was then redissolved in NaOH solution (3.75 g in 56 mL of water). KMnO_4 (7.5 g) was added to the solution, and the mixture was refluxed overnight. The brown mixture was filtered through Celite, washed with boiled water, precipitated using concentrated HCl to give white powders (2.6 g, 72%). ^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, and 119.2.

Dimethyl 2,5-dibromoterephthalate (II-1)

Concentrated H_2SO_4 (1 mL) was added to a mixture of 2, 5-dibromoterephthalic acid (7.00 g, 21.6 mmol), ethanol (80 mL) and refluxed for 8 h. The white mixture was

cooled to room temperature and the precipitated was collected. The white solid was recrystallized in dichloromethane/methanol. Yield (6.90 g, 90%). Mp: 140 °C (DSC); ^1H NMR (300 MHz, DMSO- d_6) δ 8.08 (s, 2 H), 3.87 (s, 6 H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 164.25, 135.95, 135.26, 118.95, 53.00.

2,5-Dibromo-1,4-dibenzoylbenzene (II-2)

A suspension of 2,5-dibromoterephthalic acid (1.00 g, 3.09 mmol) and thionyl chloride (0.7 mL, 9.3 mmol) in chloroform (7 mL) was refluxed for 4h. Solvents were evaporated by vacuum. The crude acyl chloride was dissolved in benzene (ca. 6 mL) and added slowly to a solution of aluminum chloride (1.00 g, 7.5 mmol) in benzene (15 mL). The yellow mixture was refluxed overnight. The yellowish mixture was poured into water, acidified with concentrated HCl, and extracted twice with ethyl acetate. After rotor-evaporated and purified by column (10% ethyl acetate in hexane) red solids were obtained (0.40 g, 30%), mp 189 – 193°C; IR (neat) 1669 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 7.87 (s, 2H), 7.84 (d, 4H), 7.74 (t, 2H), 7.61 (t, 4H); ^{13}C NMR (75 MHz, DMSO- d_6) δ_{C} 193.84, 143.42, 135.33, 135.12, 133.01, 130.50, 129.68, 118.35.

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 (II-3)

2,5-Dibromoterephthalic acid (1.00 g, 3.09 mmol) and thionyl chloride (10 mL) were heated to a reflux for at least 3 h (completely dissolved). Thionyl chloride was rotor-evaporated to give 2, 5-dibromoterephthaloyl dichloride. Under argon atmosphere, to a solution of cholesterol (2.30 g, 6 mmol) and 2, 5-dibromoterephthaloyl dichloride (0.50 g, 1.4 mmol) in toluene (40 mL), benzyltriethylammonium chloride (0.25 g, 10% mole) was added. The mixture was heated at 90 °C for at least 10 h. 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 (0.90 g, 62 %). 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.

N-Hexyl-4,4'-dibromodiphenylamine¹⁷

In a two-necked flask, 4,4'-dibromodiphenylamine (20.00 g, 61.2 mmol) and potassium *tert*-butoxide (10.0 g, 89.1 mmol) were placed and 360 mL of dry THF was added. After stirring for one hour at room temperature under argon atmosphere, 1-bromohexane (13.20 g, 80 mL) was added to solution and it was stirred for 24 hours at 60 °C. The progress of reaction was monitored by TLC. The reaction mixture was then cooled down to room temperature, poured in water and extracted with chloroform. The combined organic layers were washed with water for few times, dried over MgSO₄ and the solvent was evaporated. The crude product was purified by column chromatography (silica, hexane/chloroform = 2:1, v/v) to give 24.1 g (96%). ¹H NMR (300 MHz, CDCl₃) δ 7.33 (d, 4H), 6.80 (d, 4H), 3.60 (t, 2H), 1.60 (m, 2H), 1.32-1.27 (m, 6H), 0.87 (t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 146.74, 132.26, 122.56, 113.84, 52.45, 31.58, 27.21, 26.69, 22.63, 14.01.

*4,4'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine*¹⁷

In a flame-dried, round-bottomed flask, *N*-hexyl-4,4'-dibromodiphenylamine (5.00 g, 12.2 mmol) and dry THF (100 mL) were charged under argon. At -78 °C, *n*-

butyllithium (14 mL, 2.5 M in hexane) was then added dropwise. After stirring for 2 hours at $-78\text{ }^{\circ}\text{C}$, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.00 g, 59.0 mmol) was added, and the mixture was warmed up to room temperature and stirred overnight. The resulting milky white mixture was poured into water, extracted with ether three times and then dried over MgSO_4 . The solvent was evaporated and the residual light yellow solid was recrystallized from hexane to provide the final product as white crystals (3.87 g, 80%). Mp: $164\text{--}166\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, 4H), 7.03 (d, 4H), 3.75 (t, 2H), 1.60 (m, 2H), 1.32 (s, 24H), 1.24 (m, 6H), 0.86 (t, 3H).

General Procedure for Polymerization

In a 25 mL, two-necked round-bottomed flask equipped with a condenser and an argon purge line, dibromide monomer (1.0 mmol), diboronic acid monomer (1.0 mmol) and terakis(triphenylphosphine)palladium(0) (0.5 mol%) were placed and stirred under argon for few minutes. To this mixture, degassed toluene (20% of concentration) was added and the mixture was purged with argon for another 10 min, then heated slowly to $90\text{--}100\text{ }^{\circ}\text{C}$ to dissolve all the starting materials. A solution of sodium carbonate (7.0 mmol in 1.5 mL of water) was then added followed by the addition of 2-3 drops of aliquot 336. The reaction mixture was heated at the same temperature for 24 hours while the light yellow solution turned to light green and viscous mixture. With cooling, it was precipitated in methanol, then filtered and dried.

Polymer II-4

Starting with **II-1** (0.504 g, 1.0 mmol), 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine (0.505 g, 1.0 mmol) and a Pd catalyst (4.770 mg, 0.4 mol%), the polymer was prepared in the presence of 0.739 g of base in 5.0 mL of solvent following the procedure outlined above. A yellow precipitate was obtained: 0.612 g; IR (neat, cm^{-1}): 3020-2851 (C-H, aromatic and aliphatic), 1724 (C=O, ester), 1604 (C=C); ^1H NMR (300 MHz, CDCl_3): δ 7.91 (s, 2H), 7.69 (d, 2H), 7.63 (d, 2H), 7.47 (d, 2H), 7.17 (d, 2H), 3.74 (s, 6H), 1.79-1.64 (m, 10H), 1.37 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.50, 147.35, 140.72, 140.09, 138.09, 133.17, 132.08, 128.79, 127.87, 127.42, 126.95, 126.34, 121.15, 77.43, 77.01, 76.59, 52.34, 31.68, 26.81, 22.71, 14.07.

Polymer II-5

Starting with 0.504 g (1.0 mmol) of **II-1**, 0.558 g (1.0 mmol) of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) and 4.770 mg (0.4 mol%) of the Pd catalyst, the polymer was prepared in the presence of 0.739 g of in 4.2 mL of solvent following the procedure outlined above. An off-white precipitate was obtained: 0.830 g; IR (neat, cm^{-1}): 2925-2852 (C-H, aromatic and aliphatic), 1732 (C=O, ester), 1606 (C=C); ^1H NMR (400 MHz, CDCl_3): δ_{H} 7.98 (s, 2H), 7.88-7.81 (m, 4H), 7.70 (s, 2H), 7.61-7.54 (m, 4H), 3.81 (s, 6H), 2.21-1.16 (m, 28H), 0.85 (t, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 168.29, 151.82, 140.99, 140.28, 139.47, 133.13, 132.28, 128.88, 127.04, 126.09, 125.55, 121.50, 120.15, 77.47, 77.04, 76.62, 55.39, 52.46, 40.56, 31.82, 30.34, 30.09, 29.28, 23.91, 22.64, 14.12, 1.05.

Polymer II-6

II-2 (0.444 g, 1.0 mmol), 4,4'-bis(4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine (0.505 g, 1.0 mmol), and catalyst (4.770 mg, 0.4 mol%) were dissolved in a base solution (0.74 g in 2 mL of H₂O). Polymer was obtained as yellow solids: 0.520 g; IR (neat, cm⁻¹) 3031-2856 (C-H, aromatic and aliphatic), 1664 (C=O, ketone), 1598 (C=C); ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, 4H), 7.68 (s, 2H), 7.46-7.41 (t, 2H), 7.34-7.28 (t, 4H), 7.20-7.17 (d, 4H), 6.62-6.59 (d, 4H), 3.51 (m, 2H), 1.45-1.36 (m, 2H), 1.28-1.25 (s, 6H), 0.91-0.87 (t, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 198.62, 147.33, 139.13, 137.09, 132.99, 131.65, 129.96, 129.93, 128.18, 120.77, 52.00, 31.59, 27.23, 26.63, 24.87, 22.63, 14.04.

Polymer II-7

II-2 (2.00 g, 4.5 mmol) was added to 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (2.53 g, 4.5 mmol), a Pd catalyst (30.5 mg, 0.4 mol%) and 3.4 g of the base in 14 mL of solvent. The subsequent workup give yellowish white solids: 2.73 g; IR (neat, cm⁻¹) 3060-2854 (C-H, aromatic and aliphatic), 1668 (C=O, ketone), 1596 and 1461 (C=C); ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, 4H), 7.60 (s, 2H), 7.57-7.25 (m, 12H), 1.71-1.63 (m, 6H), 1.24-1.17 (m, 20H), 0.98 (m, 4H), 0.86-0.82 (t, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 198.46, 151.42, 140.69, 140.03, 139.78, 137.93, 136.42, 133.29, 129.94, 128.83, 128.23, 127.93, 123.35, 120.00, 55.07, 40.21, 31.84, 31.63, 30.19, 29.49, 29.31, 29.01, 23.60, 22.65, 22.45, 14.10.

Polymer II-8

To a solution of bromobenzene (1.65 mL, 15 mmol) in 50 mL of dry THF, *n*-butyl-lithium (6.0 mL, 15 mmol of 2.5 M) was added dropwise under the protection of argon at -78 °C. The solution was continued to stir for 3h. The phenyl lithium solution was added dropwise to the solution of **II-6** (0.40 g, 0.74 mmol in 10 mL of dried THF). The temperature was allowed to reach room temperature and stirred for at least overnight. The reaction progress was monitored by TLC. The light yellow solution was poured into NH₄Cl solution (50 mL), washed twice with water, extracted with chloroform and precipitated in methanol to give white solids: 0.370 g; IR (neat, cm⁻¹) 3534 (OH), 3060-2856 (C-H, aromatic and aliphatic), 1599 (C=C); ¹H NMR (300 MHz, CDCl₃) δ 7.28-7.24 (m, 22H), 6.69-6.59 (m, 8H), 3.55 (m, 2H), 3.299 (s, 2OH), 1.57 (m, 2H), 1.28 (s, 6H), 0.92-0.87 (t, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.45, 146.57, 143.88, 138.42, 134.51, 133.73, 130.41, 128.04, 127.79, 127.20, 119.99, 83.24, 52.97, 31.27, 27.23, 26.66, 22.65, 14.07.

Polymer II-9

To a solution of bromobenzene (1.25 mL, 12 mmol) and dry THF (30 mL), *n*-butyl-lithium (2.5 M, 4.8 mL, 12 mmol) was added dropwise under the protection of argon at -78 °C. The yellow-orange solution was allowed to stir at present temperature for 2 h. To the solution of **II-7** (150.55 mg, 0.23 mmol) in 6 mL of dried THF at -78 °C, the phenyllithium was added via syringe and the brown solution was slowly brought up to room temperature and stirred overnight. The yellow solution was quenched with aqueous NH₄Cl, extracted three times with chloroform, washed twice with water and the organic layer was concentrated and precipitated in methanol to give light pink solids: 0.144 g; IR

(neat, cm^{-1}) 3548 (OH), 3061-2855 (C-H, aromatic and aliphatic), 1600 (C=C); ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.25 (m, 26H), 6.70-6.55 (m, 4H), 3.56 (m, 2H), 3.31 (s, 2H), 1.56 (m, 2H), 1.29 (s, 8H), 0.93-0.89 (t, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.82, 143.33, 140.75, 139.58, 138.79, 138.79, 135.21, 128.10, 127.79, 127.25, 123.81, 119.34, 83.25, 55.01, 39.71, 31.92, 30.12, 29.47, 29.32, 23.90, 22.68, 14.14.

Polymer II-10

Starting with **II-3** (1.061 g, 1.0 mmol), 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine (0.505 g, 1.0 mmol) and a catalyst (4.770 mg, 0.4 mol%), the polymer was prepared in the presence of 0.739 g of base in 5.0 mL of solvent following the procedure outlined above. A yellow precipitate was obtained: 0.850 g; IR (neat, cm^{-1}) 2936-2867 (C-H, aromatic and aliphatic), 1717 (C=O, ester), 1600 (C=C); ^1H NMR (300 MHz, CDCl_3): δ 7.72 (s, 2H), 7.35-7.30 (d, 4H), 7.16-7.08 (d, 4H), 5.37 (s, 2H), 4.70 (m, 2H), 3.76 (m, 2H), 2.23-0.55 (m, 99H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.99, 147.32, 140.06, 139.43, 136.08, 133.81, 133.05, 131.54, 129.59, 122.82, 120.45, 117.69, 83.39, 75.04, 56.68, 56.13, 52.39, 50.00, 42.31, 39.71, 39.54, 37.71, 36.92, 36.58, 36.20, 35.81, 31.85, 31.80, 31.68, 28.25, 28.02, 27.41, 26.93, 26.80, 24.86, 24.28, 23.84, 22.84, 22.73, 22.59, 21.04, 19.33, 18.73, 14.13, 14.08, 11.88.

Polymer II-11

Starting with **II-3** (1.061 g, 1.0 mmol), 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (0.558 g, 1.0 mmol), and 4.770 mg (0.4 mol%) of a catalyst, the polymer was prepared in the presence of 0.739 g of base in 4.2 mL of solvent following

the procedure outlined above. A grey precipitate was obtained 0.635 g; IR (neat, cm^{-1}) 2930-2853 (C-H aromatic and aliphatic), 1727 (C=O, ester), 1464 (C=C); ^1H NMR (300 MHz, CDCl_3) δ 7.85-7.80 (m, 4H), 7.71-7.43 (m, 4H), 5.29 (m, 2H), 4.64 (m, 2H), 2.16-0.52 (m, 121H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.01, 151.36, 140.99, 140.16, 139.24, 134.21, 131.50, 127.68, 122.83, 119.62, 77.60, 75.47, 56.67, 56.15, 55.31, 50.00, 42.28, 40.44, 39.70, 39.52, 37.74, 36.88, 36.52, 36.19, 35.80, 31.96, 31.87, 31.80, 30.49, 29.68, 29.58, 28.23, 28.02, 27.42, 24.26, 23.85, 22.82, 22.77, 22.68, 22.57, 21.02, 19.17, 18.71, 14.19, 14.13, 11.84.

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CHAPTER 3

Fluorescence Property and Explosive Sensing

III.1 Photophysical Properties

The photophysical properties, mainly absorption and fluorescence, of the polymers are important for optical sensing of explosives and should be fully characterized prior to sensing study. All the synthesized polymers (Figure III.1) were subjected to spectroscopic studies for their absorption and fluorescence in chloroform solution and in solid film. As summarized in Table III.1, the N-hexyldiphenylamine-based polymers (**III-4**, **6**, **8**, and **10**) absorb at a higher wavelength than the fluorene-based polymers (**III-5**, **7**, **9**, and **11**). The absorption spectra of the polymers containing the N-hexyldiphenylamine moiety have two bands arising from π - π^* and charge-transfer (CT) transitions (Figure III.2). The n - π^* transition originating from the diphenylamine moiety in the polymer backbone appears at ~ 300 nm and partly overlaps with the π - π^* transition^{1,2}. The n - π^* transition is described approximately as promotion of an electron from a ‘non-bonding’ (lone-pair) n orbital to an ‘anti-bonding’ π^* orbital³.

The photoluminescence (PL) spectra for the polymers were taken under excitation of 350 nm (N-hexyldiphenylamine series) and 310 nm (fluorene series). The N-hexyldiphenylamine series of polymers emit a yellow to green color (504-532 nm) upon photo excitation in solution and as a film. The PL wavelength remains unaltered even when excitation is at a lower wavelength, indicating that energy transfer to the lowest excited state (CT) is efficient. In comparison, the PL spectra of the fluorene-based polymers (438-475 nm) are blue shifted, due to the presence of a conjugated, higher-energy fluorene moiety and the lack of donor-acceptor transfer (except for polymer **II-7** which has a charge transfer due to the benzophenone moiety)⁵.

The absolute PL quantum yield (QY, Φ_F), which is defined as the number of photons emitted in PL per absorbed photon, of polymer films was measured using integrating sphere (at the Changchun Institute of Applied Chemistry, Changchun, China). The quantum yields of the polymers containing the N-hexyldiphenylamine moiety range from 7 to 16 %. The quenching by the amine group is believed to be a main cause of low QY. Thus, the fluorene-based polymers have relatively higher quantum yields, ranging from 46 to 61%. Polymer **II-7** has a much lower QY within the series, because of the energy transfer of the excited state to the benzophenone moiety within the polymer (as in a similar case for polymer **II-6**). Clearly, polymers with high QY are ideal for fluorescence sensing of explosives.

Figure III.1. Structures of polymers synthesized in this work

Figure III.2. Absorption and emission spectra of the films of polymers II-4 to II-11. The excitation wavelength was the maximum absorption of each polymer.

Table III.1. Photophysical data for polymers **II-4** to **II-11**.

	Abs λ_{max} (nm)^a	PL λ_{max} (nm)^b	Φ_{F}^c
II-4	350	532	0.07
II-6	380	580	0.06
II-8	330	460	N/A
II-10	350	504	0.16
II-5	310	451	0.46
II-7	340	475	0.13
II-9	325	460	0.61
II-11	310	438	0.61

^a Maximum absorbance of polymers in chloroform.

^b Maximum emission of polymer film.

^c Quantum yield of polymer film.

Since the polymers will be incorporated into fibre-optic sensors for explosive sensing, the polymers need to be applied onto the small surface area of the optic fibre as a thin film. The PL profile of a film may depend on the film thickness, substrate and processing methods. Thus, the PL spectra of polymer films on optic fibre and glass were taken and compared (Figure III.3), only using polymers containing the methyl and cholesterol ester moieties (**II-4**, **II-5**, **II-10**, and **II-11**). The film on fibre was prepared by dipping and much thinner than the one spin coated on glass substrate. The emission profiles of polymers **II-4** and **II-10** are red shifted, relative to those of polymers **II-5** and **II-11**, and appear to be similar in shape and position for the films coated on optic fibres and on glass. The two measurement methods therefore give the very similar spectral results. However, the PL spectra of polymers **II-5** and **II-11** are quite different, between the two films with different thickness. The spectral broadening for the thin film on fibre is obvious, indicating the presence of polymer chain stacking. The chain stacking is likely

promoted by the large rigid cholesterol side chain within the relatively thinner film on fibre.

Figure III.3. Emission spectra of polymers **II-4** to **II-5** and **II-10** to **II-11**. (A) Thin films on the side wall of the fibre made by dipping (1.5 mg/mL) and (B) Spin coated films onto glass substrate with a thickness of approximately $6.5 \times 10^{-2} \mu\text{m}$.

Polymers containing tertiary alcohol pendent groups (**II-8** and **II-9**) were excluded in the fiber-optic PL analysis because they were found to be unstable under ambient light and/or the excitation light and PL signal fluctuation was observed. They are likely to undergo constant photo-oxidation/reduction reaction due to the unstable σ -bond at the $-\text{OH}$ position and the formation of relatively stable trityl radical when exposed to

ambient light. Figure III.4 shows a gradual decrease in PL of polymer **II-8** over 25 minutes after four excitation exposures at 330 nm in a fluorimeter.

Figure III.4. PL spectra of thin film of polymer **II-8** under ambient light over time.

Polymers containing ketones pendent groups (**II-6** and **II-7**) were also excluded from the fibre-optic PL analysis, simply because they did not exhibit any useful PL property and were mainly used for comparison and as an intermediate in synthesis.

III.2 Film Preparation and Sensing Setup

As shown above, the film thickness can affect the PL profiles of some polymers and therefore the film preparation is important for sensing study. In addition, since the analyte vapor must diffuse into the sensory films for effective detection. Thus, the dependence of fluorescence quenching on the thickness of polymer films can provide qualitative insight into the diffusion of analyte in the film. Figure III.5 illustrates the

fluorescence quenching (FQ) as measure of the percentage decrease in fluorescence intensity with respect to the film thickness.

Figure III.5. A schematic illustration of film-thickness effect on the fluorescence quenching displayed by nitro-containing compounds (Adopted from Ref. 11).

The thin film should ideally correspond to only 2-3 layers of the polymer deposited on substrate. Thus, the thin films can be quenched effectively with only surface-bound analytes, and the role of diffusion within the films is negligible. However, for a thicker film, combination of slow diffusion of the nitro compounds into the interior of the thicker films and the limited distance of energy migration (*vide infra*) produces lower FQ values. A thicker film can generate a higher emission level due to the unquenched underlayer that does not interact with explosive vapor, thus adversely affecting the quenching effect or sensing sensitivity.

We reasonably believe that the bulky cholesterol pendent groups in polymers **II-10** and **II-11** can create larger pores within the film that behaves similar to a “sponge” soaking up electron-poor π -accepting analytes. The resulting permeability of the cholesterol-substituted polymer film would allow the analyte to quench the polymer’s fluorescence more rapidly and efficiently compared to those with other pendent groups.

Films Coated on Glass Substrate by Casting and Spin Coating

Polymer films were cast from chloroform solution (5.0 mg in 1.0 mL) onto a glass plate (microscope slide, length = 23 mm, width = 23 mm and thickness = 1.0 mm) and allowed to slowly evaporate at room temperature for 24 h. The thickness of the films ranged from 375 to 2930 nm, as measured using a Tencor Alpha-Step 200 surface profiler

For spin coating, the polymer solution (5.0 mg in 1.0 mL) was dropped onto a glass plate (microscope slide, 23 x 23 x 1 mm³), which was then spun at 1000 rpm using a Chemat KW-4B Spin-Coater. The film thickness was approximately 65 nm.

Film Coated on Fibres by Dip Coating

A typical procedure is as follows: one drop of the polymer solution is dispensed onto the side wall of a fibre (15-cm long and 800- μ m core). Drying is done in air under ambient temperatures. The thickness of the polymer coating was estimated to be less than 6.0×10^{-2} μ m and the film uniformity was not strictly controlled. Bifurcated fibre architecture is fabricated, another two identical fibres (400 μ m core) as excited light delivery and signal receiving fibres, respectively.

Setup and Measurement for Explosive Sensing Using Films Coated on Glass

The setup for explosive sensing using polymer films coated on glass slides is simple to assemble, convenient to use and also reliable to quickly screen and test polymer samples. The polymer films coated on glass slides are placed in a 20-mL glass jar with a cover containing the powders of 2,4-DNT (at the bottom of the chamber) for a given period of time before taking out for immediate fluorescence measurements. Care should be taken that the polymer film is not in direct contact with 2,4-DNT powders.

Setup and Measurement for Explosive Sensing Using Films Coated on Fibres

The experimental setup is shown in Figure III.6. Ar⁺ laser power is sent to sensing segment via i-fiber to excite polymer layer. The polymer is coated on the side wall of the sensing segment, which is excited in principle by evanescent-wave (EW) of the modes formed by the coming Ar⁺ laser light. Part of the fluorescent emission is tunneled back to the sensing segment and coupled into r-fiber and sent to the spectrometer-computer system for analysis. The Ar⁺ laser power after i-fiber is adjusted to about 0.51 mW or lower. Weaker and pulsed form of excitation light is required to avoid the fluctuation of fluorescent emission. The light On/Off switch is manually controlled to generate the pulse.

DNT is placed in a small glass bottle with the size of 40 mm x 50 mm. A 10mm hole is bored in the center of the cap to allow the sensing segment to enter. Since only the bottle is moving, all optical components of the sensing system remains the same state during the entire measurement, the signal fluctuation maybe caused by the position change of the components is eliminated. LVF (Ocean Optics Inc.) is a linear variable

optical filter to remove the stray excitation light as much as possible. USB 2000 is a palm-held spectrometer (Ocean Optics Inc.)

Figure III.6. Experimental setup for fiber-optic sensing of explosives. i-fiber: illuminating fiber; r-fiber: receiving fiber. LVF: linear variable filter; MMF: multimode fiber; Light On/Off switch: On only when performing data acquisition, Off when waiting. The purpose of this switch is to avoid polymer deterioration caused by excitation power. Polymer A: polymer films coated on 20-mm long fiber side wall.

The sensing experiment 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 DNT container is carefully sliding to the sensing segment until all the polymer coated fiber tip is inside the container. Immediately the spectrum is recorded as

the first quenching spectrum. This spectrum should be the same as the ones before quenching.

3. Following the step 1, the spectrum is recorded every minute. The observed fluorescent emission should drop continuously for each spectrum. Overlaying them with those before quenching, the quenching efficiency can be estimated.

III.3 Explosive Sensing Study

Immediately after exposing the polymer film to the analyte (2,4-DNT) for a specific period of time, the fluorescence spectra were recorded on a fluorimeter at the excitation wavelength of 350 nm for polymers **II-4** and **II-10** and 310 nm for polymers **II-5** and **II-11**, respectively. The data with an average of two readings are reported. The equilibrium vapour pressure of DNT is assumed to be 1.74×10^{-4} mmHg at 25 °C according to the documented value⁷. Quenching efficiency is defined as $(I_0 - I)/I_0 \times 100$, where I_0 is the initial fluorescence intensity.

Rapid photoluminescence quenching was observed for all four polymer films upon exposing to DNT vapour. Figure III.7 shows changes in fluorescence intensity of polymer **II-10** film (6.5×10^{-2} µm thick) upon exposure to DNT vapour over several different time periods. With a 60-second exposure, quenching efficiency was about 25% (inset, Figure III.7) and reached 70% after 600 seconds of exposure to DNT vapour.

Figure III.7. Time-dependent fluorescence intensity of the film (6.5×10^{-2} μm thickness) of polymer **II-10** upon exposure to DNT vapour at room temperature ($\lambda_{\text{ex}} = 350$ nm).

Figure III.8 shows the time-dependent fluorescence intensity of the films of polymers **II-4**, **II-5**, **II-10** and **II-11** (6.5×10^{-2} μm thickness), under constant ambient pressure, to DNT vapour measured by a fluorimeter and using a fibre-optic probe. The trends in the results obtained by both sensing methods are almost identical. Polymer **II-10** shows the highest quenching efficiency, 48 % within 25 seconds for fibre-optic probe and 55 % within the first minute for free-standing film, follow by **II-11** and **II-5**. It is interesting to see that no shift in the emission wavelength occurred upon analyte exposure, indicating that exciplexes were not formed. The emission intensity of exposed films is regained after standing in air, which shows the binding of the analyte and the quenching process is reversible.

Figure III.8. Fluorescence intensity quenching of polymers **II-4**, **5**, **10**, and **11**; (A) Films spin-coated with thickness of 6.5×10^{-2} μm coated on glass; (B) Films deposited on fibre-optic probes with a solution concentration of 1.5 mg/mL.

All the polymers (**II-4**, **II-5**, **II-10**, and **II-11**) showed remarkable nitroaromatic detection capability (Table III.2). In particular, green luminescence (504 nm) of the film of **II-10** is rapidly quenched when exposed to DNT vapour, by 55 % in the first one minute and 70 % in two minutes. In comparison, the fluorescence of the film of **II-4** on glass is quenched by 23% in one minute and 45% in two minutes. This difference in quenching efficiency is due to the difference in polymer film morphology that is related to the size of pendent ester groups in the polymers. The two bulky cholesterol moieties within each repeat unit of polymer **II-10** is believed to be able to increase the free volume or porosity of thin films, which allows the DNT vapour to penetrate deeper in and better interact with the polymer chains.

Comparison of polymers **II-5** and **II-11** reveals that the sizes of pendent ester groups have no dramatic effect on the quenching efficiency toward DNT vapour. Both films of polymers **II-5** and **II-11** on glass plates showed roughly 40 % quenching after 1 min and 60 % after 2 min exposure to DNT vapour. The long alkyl groups on the fluorine

moiety of these two polymers may have override or level off the effect of the ester group, making them equally good “sponge” materials for absorbing and sensing nitroaromatic explosives. It is very interesting to see that polymer **II-5** with such a simple structure can have the sensing property as good as the pentiptycene containing polymer reported by the MIT group¹⁰.

Table III.2. Changes in fluorescence intensity of the films of polymers **II-4**, **5**, **10**, and **11** coated on glass and optic fiber quenched by DNT.

Time (sec)	% Change in fluorescence intensity of film coated on glass quenched by DNT				% Change (time) in fluorescence intensity of film coated on optic fiber quenched by DNT			
	II-4	II-10	II-5	II-11	II-4	II-10	II-5	II-11
60	23	55	41	46	31 (15 s)	48 (25 s)	26 (10 s)	15 (20 s)
120	45	70	60	60	38 (23 s)	57 (30 s)	74 (62 s)	36 (32 s)
300	64	78	81	72	44 (43 s)	60 (35 s)	87 (133 s)	48 (40 s)
600	75	87	96	88	46 (78 s)	62 (45 s)		57 (48 s)
								63 (83 s)
								70 (106 s)
								76 (184 s)

Polymers **II-10** and **II-11** both contain the large pendent cholesterol group and the former has a slightly better quenching efficiency than the latter (55 % vs. 46% in 1 min, Table III.2). Since the pendent groups are the same, it can be assumed that the N-hexyldiphenylamine and the substituted fluorine moieties impart the similar free volume to the polymer.

Although a good fluorescence quenching in **II-10** may be related to a stronger polar-polar interaction between the electron-donating amine moiety and the electron-accepting DNT molecules, its relatively low quantum efficiency (Φ_F 0.16) makes it less useful for actual sensor device application than polymer **II-11** with a much higher quantum yield (Φ_F 0.61), when the overall power efficiency and other device design factors are concerned. Considering all the factors including the synthesis, cost and performance, polymers **II-5** and **II-11** are the best candidates among all the synthesized polymers in this thesis work, for TNT sensing.

III.4 Conclusion

The two new series of fluorescent polymers having the fluorene and diphenylamine units in the polymer backbone have been successfully synthesized through the Suzuki cross-coupling reaction. Absorption and photoluminescence of N-hexyldiphenylamine-based polymers (**II-4**, **6**, **8**, **10**) are red shifted due to the donor-acceptor interaction in comparison with the fluorine-based series of polymers (**II-5**, **7**, **9**, **11**). The latter series have much higher PL quantum efficiencies, as their rigid conjugated backbone provides an effective exciton delocalization.

The explosive detection sensitivity can be correlated to the polymer structures and both the pendent groups and the units in the main chain can affect or contribute to the free volume of the polymer films. The polymers with large pendent groups and rigid bulky backbone show excellent fluorescence quenching efficiency. The explosive sensing performance of some polymers is equal or better than the best reported polymers to date.

Considering the synthetic routes, costs and sensing performance, polymers **II-5** and **II-11** are the best candidates among all the synthesized polymers for TNT sensing and for further application in fibre-optic sensors.

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APPENDIX A

^1H and ^{13}C NMR Spectrums of Monomers II.1 to II.3 and Intermediates

Figure A.1. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of 1, 2-dibromo-2,5-dimethylbenzene.

Figure A.2. ^1H NMR (300 MHz, DMSO) and ^{13}C NMR (75 MHz, DMSO) spectra of 2, 5-dibromoterephthalic acid.

Figure A.3. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of dimethyl-2,5-dibromoterephthalate (II-1).

Figure A.4. ^1H NMR (300 MHz, DMSO) and ^{13}C NMR (75 MHz, DMSO) spectra of (2,5-dibromo-1,4-phenylene)bis(phenylmethanone) (II-2).

Figure A.5. ^1H NMR (300 MHz, CDCl_3) spectrum of compound II-3.

Figure A.6. ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound x.

Figure A.7. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of N-hexyl-4,4'-dibromodiphenylamine.

Figure A.8. ¹H NMR (300 MHz, CDCl₃) spectrum of 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-hexyldiphenylamine.

APPENDIX B

^1H and ^{13}C NMR Spectrums of Polymers II.4 to II.11

Figure B.1. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-4.

Figure B.2. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-5.

Figure B.3. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-6.

Figure B.4. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-

Figure B.5. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-8.

Figure B.6. ¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectra of polymer II-9.

Figure B.7. ^1H NMR (300 MHz, CDCl_3) spectra of polymer II.10.

Figure B.8. ^{13}C NMR (75 MHz, CDCl_3) spectra of polymer II.10.

Figure B.9. ^1H NMR (300 MHz, CDCl_3) spectra of polymer II.11.

Figure B.10. ^{13}C NMR (75 MHz, CDCl_3) spectra of polymer **II.11**.