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Detection of nitroaromatic compounds based on photoluminescent side chain polymers

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ABSTRACT

The synthesis, spectroscopic characterization and fluorescence quenching efficiency of a polymer (PSt-NI) and a low molecular weight molecule (NI) containing the 4-(N, N disubstituted)amino-N-2,5ditertiobutylphenyl-1,8-naphthalimide chromophore are reported. Similar spectroscopic properties of thin films and solutions are observed. This is consistent with the absence of interactions between polymer side chains. The absorption and fluorescence spectra of PSt-NI studied in various solvents of different polarity are compared to the corresponding spectra of NI. The longest wavelength absorption of PSt-NI and NI is characterized by a band with a maximum wavelength around 410 nm. The peak position is sensitive to the polarity of the solvent, which is in agreement with the charge transfer character of the transition. The fluorescence spectrum of PSt-NI shows a maximum emission in chloroform at 515 nm and is red shifted compared to those of NI. Fluorescence lifetimes of PSt-NI and NI are measured in presence and absence of 2,4-dinitrotoluene (DNT) and the results are interpreted via the Stern-Volmer analysis. In solution, the fluorescence quenching of NI is purely collisional, whereas both dynamic and static quenching are observed with PSt-NI. Upon 1 minute exposure to DNT vapor, it was shown that a 5 nm thick film of PSt-NI exhibited a 45% drop in its fluorescence intensity, which makes this polymer very attractive for sensing applications.

Keywords: optical sensor, fluorescent polymer, nitroaromatic compound detection, naphthalimide, Stern-Volmer, fluorescence quenching.

INTRODUCTION

In a context of growing international terrorism, there is today an increasing need for highly sensitive smart sensors able to detect and identify clearly and rapidly hazardous substances and more particularly explosives. In this domain, canine detection ability appears very powerful (in the part-per-trillion range). However, in addition to be time consuming, use of dogs for locating explosives has a limited reliability [1]. This is partly linked to the dog's desire for getting reward anyway. As commonly used high explosives have low vapor pressure, efficient ultra trace explosive detection requires the development of highly sensitive sensors which have in addition to allow speed and selectivity. Today, many different analytical methods for detecting trace explosives in the luggage and on travellers have been proposed and have been recently compared and discussed from a quantitative point of view by M. Nambayah *et al.* [2]. Some devices are already commercially available. They are mainly based on the use of ion mobility spectrometry (IMS) technology [3], surface acoustic wave (SAW) sensor with chemoselective polymers as sensitive layers [4] or in conjunction with a gas chromatograph [5], and finally fluorescence quenching of Π conjugated fluorescent polymer [6]. The latter approach seems particularly promising since it has shown a limit of detection as low as 1fg of 2,4,6-trinitrotoluene (TNT) in laboratory conditions using just spontaneous emission₆ and has demonstrated an improvement in sensitivity by a factor of 30 when the Π conjugated polymer is optically pumped at intensities near its lasing threshold [7].

As an alternative route to Π conjugated polymers, side chain polymers where the fluorescent moiety is linked to the polymer backbone via a spacer are particularly attractive. Firstly, as fluorescent moieties

will be able to transfer their energy to the neighbour quenching sites within the Förster radius, namely 1 nm, a significant amplification of the transduction signals is expected. Very high fluorescence quantum yield can be achieved with side chain polymers. In addition, these polymers are chemically and photochemically stable and therefore can be processed in air and are good candidates for exhibiting durability under irradiation. Finally, side chain polymers are soluble in common organic solvents, making easy their spin-coating.

Until now, little work has been devoted to side chain fluorescent polymers for chemical sensors [9] and as far as we know, nothing has been done in the polynitroaromatic detection field. Thus our aim here is to assess the concept of side chain fluorescent polymer as sensitive layer of an explosive detector. TNT being the most commonly used explosive in unexploded ordnance [8], we have focused our effort on the detection of TNT traces. As the equilibrium vapor concentration of TNT is very low (70pg/mL of air at 25°C, i.e. 13.7ppt), 2,4-dinitrotoluene (2,4-DNT), an impurity of military grade TNT, with a vapor concentration of 230ppt at 25°C has been chosen as analyte in our study. Finally, N-substituted-4-amino-1,8-naphthalimide has been selected as fluorescent moiety because it is known to lead to polymers with high fluorescence quantum yield in the solid state [10]. This paper presents the photophysical properties of a polystyrene functionalised with a N-substituted-4-amino-1,8-naphthalimide chromophore (PSt-NI) measured both in the presence and absence of DNT. By way of comparison the same experiments have been done on a low molecular weight model compound derived from the same chromophore (NI) whose structure is depicted on figure 1.

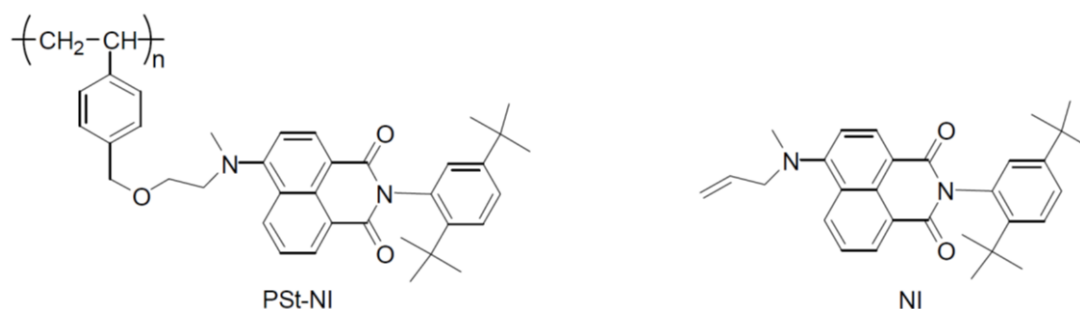


Figure 1: Molecular structure of PSt-NI and NI.

EXPERIMENTAL

Synthesis

In order to avoid Π stacking of the naphthalimide moieties which would reduce the fluorescent quantum yield, we have grafted a bulky group, namely the 2,5-ditertbutylphenyl group, onto the nitrogen atom of the imide function. Due to the presence of the tertibutyl group in the ortho position, the chromophore is no longer planar. The phenyl moiety is perpendicular to the naphthalimide group and hence moves away the polymer side chains (figure 2).

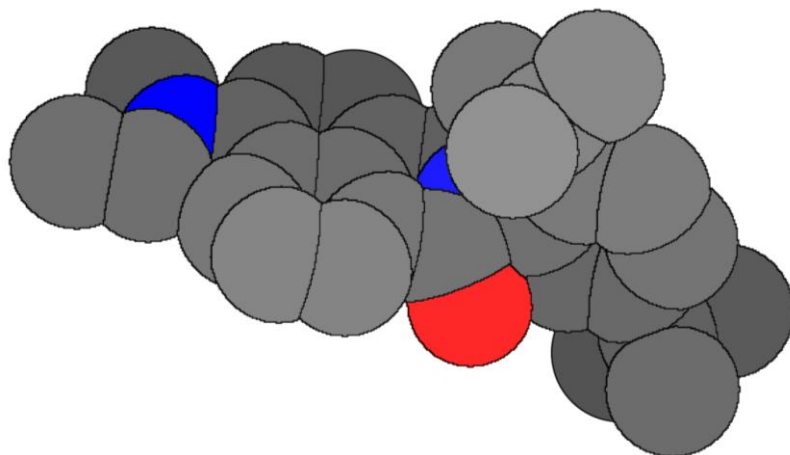


Figure 2: Space-filling model of the chromophore under study.

Figure 3 shows the synthetic pathway adopted to get PSt-NI. NI has been prepared in two steps starting from 4-bromo-1,8-naphthalic anhydride, by the procedure described in 2 synthesis.

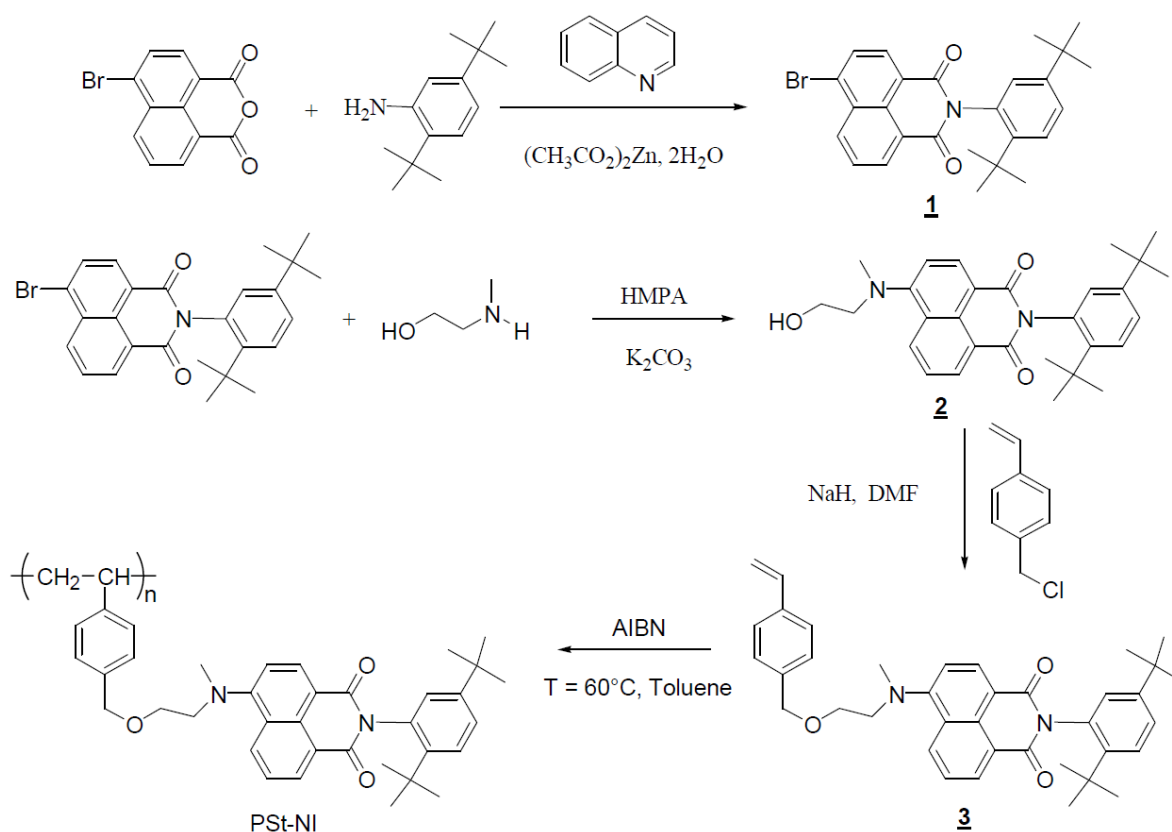


Figure 3: Synthetic pathway and chemical structure of PSt-NI.

4-bromo-N-2,5ditertibutylphenyl-1,8-naphthalimide (1) [11] :

To 27.7 g of 4-bromo-1,8-naphthalic anhydride (0.1 mol) and 41 g of 2,5-ditertibutylaniline (0.2 mol) in suspension in 125 mL of quinoline were added 6.98 g of zinc acetate (0.032 mol). The mixture was heated at reflux for 4 h. After cooling at room temperature the reaction mixture was poured in acidic water. A solid separated. The solid was collected and washed with water and ether, and dried in vacuum. The crude product was purified by column chromatography with chloroform as eluent. The product was further purified by crystallisation in hexane to give 18.5 g of **1** (yield = 40%).

$^1\text{H NMR}$ (300MHz, CDCl_3) δ : 8.7 (d, 1H), 8.6 (d, 1H), 8.5 (d, 1H) 8.1 (d, 1H), 7.9 (t, 1H), 7.6 (d, 1H), 7.5 (d, 1H), 7.0 (d, 1H) 1.31 (s, 9H), 1.27 (s, 9H)

IR (cm^{-1}) 2961 (s, C-H sp^3), 1712 (s, C=O), 1670 (s, C=O), 1588 (m, C=C)

mp : 233°C

4-(N methyl, N hydroxyethyl)amino-N-2,5ditertibutylphenyl-1,8-naphthalimide (2) :

To 15.04 g of **1** (32 mmol) and 4.85 g of freshly distilled 2-(methylamino)ethanol (65 mmol) in solution in 80 mL of distilled HMPA were added 5.29 g of potassium carbonate (38 mmol) and 2 drops of Aliquat 336. The mixture was stirred for 20 h at 80°C . After pouring in acidic water (1.5 L), the reaction mixture yielded a solid. The resulting yellow brown precipitate was removed by filtration, washed with water and dried under vacuum. The crude product was purified by column chromatography with methylene chloride as eluent to give 9.92 g (67.7%) of a yellow solid.

$^1\text{H NMR}$ (300MHz, CDCl_3) δ : 8.7 (d, 1H), 8.6 (d, 1H), 7.7 (t, 1H), 7.6 (d, 1H), 7.4 (d, 1H), 7.3 (d, 1H), 7 (d, 1H), 4.0 (m, 2H), 3.5 (t, 2H), 3.1 (s, 3H), 2 (s, 1H), 1.31 (s, 9H), 1.28 (s, 9H)

IR (cm^{-1}) 3489 (m, OH) 2928 (s, C-H sp^3), 1694 (s, C=O), 1653 (s, C=O), 1584 (s, C=C)

mp : 189°C

Monomer (3)

In an Ar atmosphere a mixture of 9.19 g (20 mmol) of 4-(N methyl, N hydroxyethyl)-N-2,5ditertiobutylphenyl-1,8-naphthalimide, 3.66 g (24 mmol) of chloromethylstyrene and 65 mL of dry DMF was cooled to 0°C. To the mixture 2 g (50 mmol) of sodium hydride (60%) were added slowly in 1 h while stirring. The reaction mixture was then stirred for 3 h at room temperature. After completion of the reaction, methanol is added carefully to destroy sodium hydride in excess. The resulting mixture is poured into acidic water. The resulting solid was isolated by filtration, washed with water and hexane. The crude product was purified by column chromatography with methylene chloride as eluent followed by crystallisation in a mixture of hexane/methylene chloride.

Yield : 6.55 g (57%) of a yellow solid

¹H NMR (300MHz, CDCl₃) δ : 8.72 – 6.97 (arom. 12H), 6.72 (q, 1H), 5.78 – 5.73 (d, 1H), 5.28 – 5.24 (d, 1H), 4.56 (s, 2H), 3.81 (t, 2H), 3.61 (t, 2H), 3.11 (s, 3H), 2 (s, 1H), 1.30 (s, 9H), 1.27 (s, 9H)

¹³C NMR (75MHz, CDCl₃) δ: 165.5 (C=O), 165.0 (C=O), 156.7, 149.8, 143.8, 137.5, 137.2, 136.4, 133.2, 132.7, 131.44, 131.38, 130.6, 128.6, 127.87, 127.81, 126.3, 126.1, 126, 125.2, 123.5, 116.1, 115, 114, (arom. C) 73.0 (φ-CH₂-O-), 67.7 (-CH₂-O-), 57.1 (-CH₂-N), 41.2 (CH₃-N), 35.5 (aliph. C), 34.2 (aliph. C), 31.7 (t-CH₃-), 31.2 (t-CH₃-)

IR (cm⁻¹) 2962 (s, C-H sp³), 2869 (s, C-H sp³), 1697 (s, C=O), 1655 (s, C=O), 1585 (s, C=C), 1238 (C-O-C)

mp : 144.7°C

Polymer (4)

PSt-NI was prepared by free radical polymerisation in solution with AIBN as initiator and toluene as solvent. A mixture of 6.5 g (11.3 mmol) of **3** and 4.63 mg (0.028 mmol) of AIBN in 65 mL of freshly distilled toluene was thoroughly degassed by the conventional freeze-thaw technique before sealing and removing from the vacuum apparatus.

Polymerisation was allowed to proceed for 24 h at 60°C. PSt-NI was isolated by precipitation into methanol and further purified by reprecipitation from methylene chloride solution into methanol.

Yield : 3.84 g (59 %)

SEC (PSt calibration) : M_w = 83 000, M_n = 43 000, M_w/M_n = 1.93

T_g = 184°C (midpoint)

4-(N methyl, N allyl)amino-N-2,5ditertiobutylphenyl-1,8- naphthalimide (NI)

This compound was similarly obtained by the procedure described in 2 synthesis

Yield : 61.3 %.

¹H NMR (300MHz, CDCl₃) δ: 8.7 (d, 1H), 8.6 (d, 1H), 7.7 (t, 1H), 7.6 (d, 1H), 7.4 (d, 1H), 7.3 (d, 1H), 7 (d, 1H), 6.1 – 5.98 (m, 1H), 5.6 – 5.35 (m, 2H), 3.97 (m, 2H), 3.05 (s, 3H), 1.31 (s, 9H), 1.28 (s, 9H)

IR (cm⁻¹) 2962 (s, C-H sp³), 1702 (s, C=O), 1662 (s, C=O), 1586 (s, C=C)

mp : 151°C

Films preparation

Thin films on glass microscope plates were formed by dissolving the polymer in chloroform ([PSt-NI] = 0.5 g/L) and spin-coating the solutions on the substrates. Each film was dried under vacuum overnight before use.

Photophysical measurements

UV/vis absorption spectra were recorded on a Varian Cary5E spectrophotometer. Corrected emission spectra were obtained on a Jobin-Yvon Spex Fluorolog 1681 spectrofluorometer. Polymer thin-film spectra were recorded by frontface (22.5°) detection.

Absolute quantum yield (ϕ_f) measurements

Measurements of the fluorescence quantum yield were carried out using an integrating sphere (from Labsphere Inc.). This sphere is hollow and coated on its internal surface with a diffusely reflecting material (reflecting efficiency: 95% in the spectral range 250-2500 nm). Photons created within the sphere are channelled, after reflections from the surface, to the exit port located at the bottom part of the sphere. The intensity detected at the exit is directly proportional to the total light flux created within the sphere. It does not depend on the angular distribution of the signal or the orientation of the emitting dipoles in the sample. A laser beam of 405 nm ((D) - Model#PPM04 from Power Technologies, power output 5 mW) is used to excite the sample placed at the centre of the sphere. In order to attenuate the pump beam and to avoid damage to the sample, a neutral filter was placed in front of the laser source.

Near normal incidence has been used for all measurements. The PL signal, scattered within the sphere, is measured at the exit with a photodiode (Hamamatsu S2281), preceded by a cutoff filter. We used a GG475 (Scott) filter (wavelength cutoff at 450 nm) to absorb the scattered excitation light.

Three measurements were performed on each sample according to the procedure described by Friend and al¹², in order to determine the PL quantum yield (ϕ_f).

The fluorescence response of the polymer films to the DNT vapor was evaluated by inserting the polymer films into a macro cell (50x30x10 mm) in quartz suprasil supplied by Hellma. This cell was closed hermetically by a PTFE lid which maintains the cover glass in vertical position in the center of the cell. For the quenching measurements fresh DNT powder was placed at the bottom of the cell and the system was left for one hour under vapor pressure of DNT to obtain an equilibrium. DNT was purchased from Aldrich Chemical CO, Inc..

RESULT AND DISCUSSION

Photophysical properties of the polymer

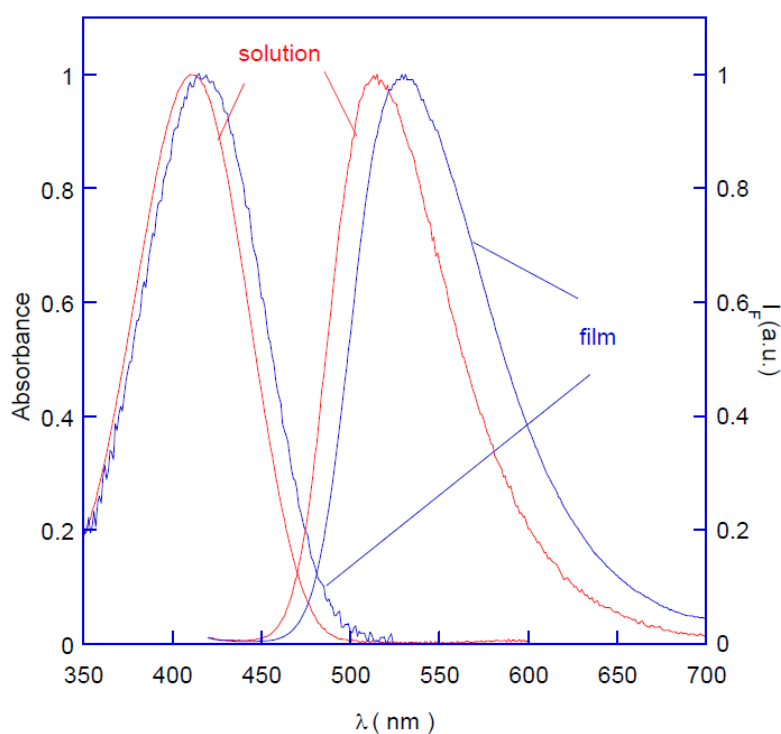


Figure 4. absorption and emission spectra of PSt-NI in chloroform and in spin-cast film

Figure 4 shows the absorption and emission spectra of PSt-NI in chloroform and in thin film. The absorption and emission characteristics of PSt-NI and NI in solvents of different polarity and PSt-NI in thin films are given in table 1. The longest wavelength absorption of the systems is characterized by a band with the maximum located at around 410 nm. This broad and unstructured band corresponds to an internal charge transfer transition from the 4-amino group to the naphthalimide ring system [13]. The peak position of the systems is strongly sensitive to the polarity of the solvent, which confirms the charge transfer character of this transition. The red shift induced by solvent polarity is more pronounced for the fluorescence maximum wavelengths than for the absorption ones, this observation suggests that in each case the emitting state is more polar than the ground state. The fluorescence spectrum of PSt-NI is more red-shifted than the emission band of its model, (16 nm for CHCl₃) this discrepancy can be attributed by a slight enhancing of the micropolarity due to the proximity of the surrounding fluorophores. Fluorescence quantum yield of PSt-NI and NI measured in a series of solvents of different polarity are collected in table 2. The fluorescence quantum yield decreases with an increase in the polarity of the medium. This decrease is most prominent in polar environment. The quantum yields of PSt-NI are similar of the corresponding monomer due to very weak interaction between the chromophores thanks to the tertibutyl groups.

Compound	Solvent	λ_{abs} (nm)	λ_{fluo} (nm)	$\Phi_{\text{F}}^{\text{b}}$
NI	Cyclohexane	393	461	
NI	Toluene	405	488	
NI	CHCl ₃	415	499	0.85
NI	THF	405	506	
NI	CH ₃ CN	417	522	
NI	DMSO	423	532	
PSt-NI	Toluene	407	509	
PSt-NI	CHCl ₃	410	515	0.62
PSt-NI	THF	407	516	
PSt-NI	Thin film			0.6

^a PSt-NI is insoluble in THF, CH₃CN and DMSO, ^b Error: 5-10%

Table 1: Absorption and Emission properties of **NI and PSt-NI** in different solvents^a

The absorption spectrum of films of PSt-NI are shapely similar to its corresponding spectra in solution. The fluorescence quantum yield in films is found to be as high as in solution. The very similar spectroscopic properties of thin films and solution of PSt-NI suggest very weak electronic interaction between the chromophores in the polymer.

Fluorescence quenching

In solution

To evaluate the interaction between the fluorophore and DNT in solution, we conducted Stern-Volmer quenching studies in chloroform. Fluorescence quenching can occur by two limiting processes : dynamic or static quenching. If the quenching is purely dynamic, the process is induced by collision between M*, the excited specie and Q, the quencher. The relative emission intensity I_0/I at a given wavelength, which is equal to the ratio of the fluorescence lifetime of the fluorophore is related to the concentration of the quencher [Q] by the Stern-Volmer equation :

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_D [Q] = 1 + k_q \tau_0 [Q]$$

where K_D (L.mol⁻¹) is the rate of the dynamic quenching and k_q (L.mol⁻¹s⁻¹) is the bimolecular quenching constant. In contrast, static quenching, resulting to a preformed complex MQ, does not

induce change of the excited-state lifetime of the uncomplexed fluorophore M. If static and dynamic quenching occur simultaneously, the fluorescence intensity ratio is given by the following equation:

$$\frac{I_0}{I} = (1 + K_Q[Q])(1 + K_S(Q))$$

where K_S (M^{-1}) is the rate of the static quenching and the fluorescence lifetime ratio is given by the following equation

$$\frac{\tau_0}{\tau} = 1 + K_Q[Q]$$

The obtained data resulting from quenching experiments of NI and PSt-NI in chloroform are gathered in table 2. Figure 5 displays the quenching of the emission spectra of PSt-NI with DNT in chloroform. For the naphthalimide fluorophore NI, the quenching is purely collisional and an electron transfer process can be considered to explain the fluorescence attenuation. The driving force of this electron transfer can be estimated from the Rehm-Weller equation [14] ($\Delta G_{eT} = E_{ox} - E_{red} - \Delta E_{00}$) neglecting the Coulomb part of the stabilization energy. In this equation, ΔG_{eT} is the variation of the standard free energy, E_{ox} and E_{red} are the oxidation and the reductive potential, and ΔE_{00} is the difference between the lowest vibrational levels of the excited state and the ground state of the fluorophore.. With the assumption of an electron transfer from N,N dialkyl anilino group of the naphthalimide ($E_{ox} = 1.06$ V vs SCE) [15] to the DNT ($E_{red} = -1.00$ V vs SCE) [16] and with a zero-zero energy transition equal to 2.94 eV in chloroform, the estimated driving force is strongly exergonic : $\Delta G_{eT} = -0.52$. In contrast both dynamic and static quenching is observed for PSt-NI. The observed static quenching might be explained by the presence of specific DNT quenching site in the polymer PSt-NI due to hydrophobic interactions.

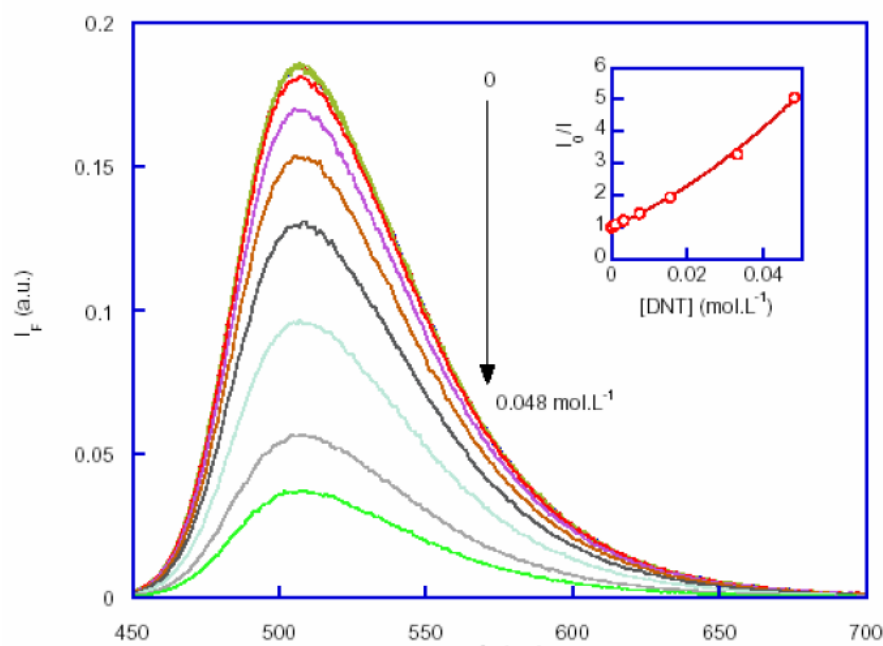


Figure 5. Quenching of the emission of PSt-NI upon addition of DNT (solvent : chloroform)

Compound	K_D ($L.mol^{-1}$)	K_S ($L.mol^{-1}$)	k_q ($L.mol^{-1}.s^{-1}$)
NI	76		$9.3 \cdot 10^9$
PSt-NI	22.4	25	$2.9 \cdot 10^9$

Table 2: Static and dynamic Stern-Volmer constants for NI and PSt-NI in chloroform.

In films

The fluorescence response of spin-cast PSt-NI film to the DNT vapors is then examined. A typical evolution of the emission spectra of a 5 nm thick film as a function of time upon DNT exposure is displayed on figure 6. A significant decrease of the fluorescence intensity is observed. After 1 minute

exposure, the intensity decreases of 45 %. It appears the kinetic of the film's response is controlled by the rate at which the DNT diffuses in the polymer films.

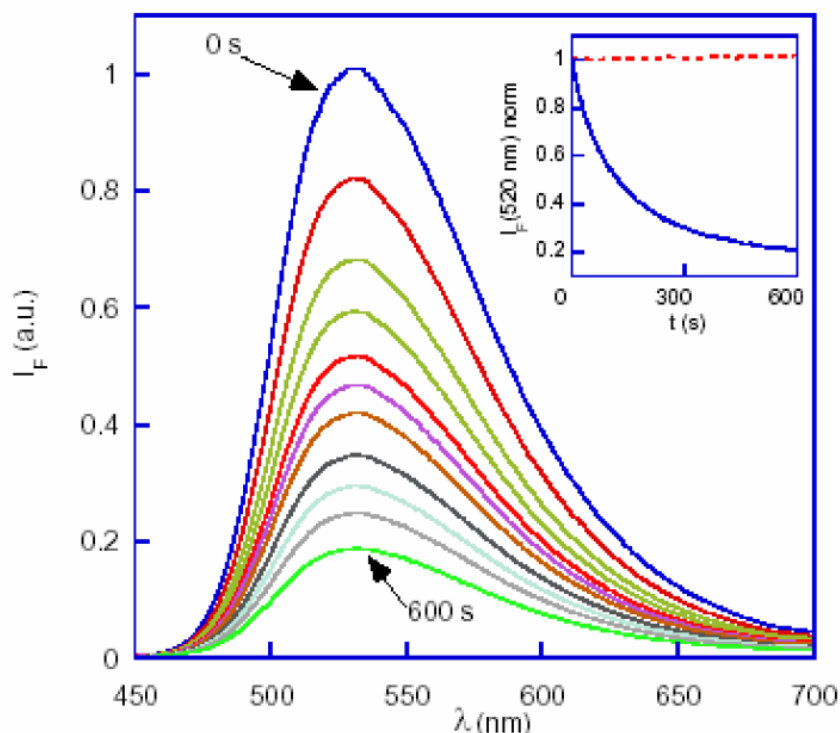


Figure 6. Quenching of fluorescence PSt-NI film in presence of 2,4 DNT vapor. Inset: fluorescence time evolution without (dashed line) and with (full line) 2,4 DNT vapor. ($\lambda_{em} = 520$ nm)

CONCLUSIONS

A polymer (PSt-NI) and a model molecule (NI) based on fluorophore have been synthesized and fully characterized. Their spectroscopic properties have been evaluated. The study of fluorescence lifetime in solution of PSt-NI and NI in presence of DNT has shown that the fluorescence quenching of NI is purely dynamic in nature and can be explained by an electron transfer process whereas in the case of PSt-NI both static and dynamic quenching are observed. Finally a thin film of PSt-NI has demonstrated a large and fast response to DNT vapor. The ability of PSt-NI to detect ultra-trace of DNT was found to be in the same order of magnitude as that of previously described systems.

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