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Perylene/PMMA Thin Films**

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Number of pages: 18

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# Fluorescence Detection of Nitrogen Dioxide with Perylene/PMMA Thin Films

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## Abstract

Thin films of polymethylmethacrylate (PMMA) doped with perylene provide selective, robust, and easily prepared optical sensor films for NO<sub>2</sub> gas with suitable response times for materials aging applications. The materials are readily formed as 200 nm thin spin cast films on glass from chlorobenzene solution. The fluorescence emission of the films ( $\lambda_{\text{max}} = 442 \text{ nm}$ ) is quenched upon exposure to NO<sub>2</sub> gas through an irreversible reaction forming non-fluorescent nitroperylene. Infrared, UV-vis, and fluorescence spectroscopies confirmed the presence of the nitro adduct in the films. In other atmospheres examined, such as air and 1000 ppm concentrations of SO<sub>2</sub>, CO, Cl<sub>2</sub>, and NH<sub>3</sub>, the films exhibited no loss of fluorescence intensity over a period of days to weeks. Response curves were obtained for 1000, 100, and 10 ppm NO<sub>2</sub> at room temperature with equilibration times varying from hours to weeks. The response curves were fit using a numerical solution to the coupled diffusion and a nonlinear chemical reaction problem assuming that the situation is reaction limiting. The forward reaction constant fitted to experimental data was  $k_f \sim 0.06 \text{ (ppm}\cdot\text{min)}^{-1}$ .

Keywords: nitrogen dioxide, optical sensor, fluorescence, perylene, nitroperylene

## 1. Introduction

The detection of nitrogen dioxide via optical sensing has received growing interest as an alternative to sensors based on electrical resistance at high temperature [1]. Various techniques have been employed, which include fluorescence [2], UV-vis absorption [3], refractive index [4], and surface plasmon resonance (SPR) [5]. The sensor materials typically consist of robust optical dyes, such as metal phthalocyanines [6], porphyrins [2], and azobenzenes [7], applied to various surfaces using Langmuir-Blodgett (LB) film deposition [8], vapor deposition [5], and dip coating [7] techniques. The sensor materials and optical platforms offer several advantages over electrical based systems, most important of which is the remote sensing capability and absence of electrical contacts, a problem for ignitable environments. A current drawback with these sensor films, however, is the poor reversibility observed at room temperature [2,5,6,8,9]. But, for specific applications where continuous  $\text{NO}_2$  evolution is concerned or for uses as dosimeters these sensor films should attract further interest.

In a particular application involving the monitoring of high explosive (HE) materials (e.g., rocket fuel, explosives) degradation, optical sensor systems are well suited for in situ detection of  $\text{NO}_x$  buildup. HE materials are commonly composed of nitrated hydrocarbons that breakdown slowly over time to release  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ , as well as other byproducts [10]. Continuous monitoring of  $\text{NO}_2$  evolution could provide a means to evaluate the level of HE material degradation. In such applications where the breakdown and release of  $\text{NO}_2$  gases as well as the storage time of the materials is on the

order of years, a robust sensor film with response times of hours to days would be suitable.

Described herein is the preparation and characterization of an inexpensive, robust, and readily prepared NO<sub>2</sub> sensor film using perylene as a fluorophore dye immobilized in a polymethylmethacrylate (PMMA) film. The film was prepared through spin casting of a PMMA/peryene solution in chlorobenzene on a glass coverslip. Upon exposure to NO<sub>2</sub> the film's fluorescence, measured at 442 nm, was quenched irreversibly. Using various spectroscopic techniques, NO<sub>2</sub> was found to react with perylene to form the non-fluorescent nitroperyene. Response times of minutes to hours were observed for concentrations above 0.1% NO<sub>2</sub> in nitrogen. At mid-to-low ppm levels of NO<sub>2</sub> the response times were long, often running into days or weeks. The fluorescence response vs. time data could be described using a predictive model involving coupled diffusion and nonlinear chemical reaction. The model provides a means to identify unknown NO<sub>2</sub> gas concentrations in static conditions and may be configured to systems involving gas evolution.

## 2. Experimental

All solvents and reagents were obtained from Aldrich in reagent grade and used as received. Tetrahydrofuran (Aldrich) used for UV-vis spectral analyses was of spectroscopic grade. For the preparation of the sensor films, perylene was dissolved in a solution of 20% PMMA (Mw = 75,000) in chlorobenzene at a concentration of 2 mM. The mixture was stirred on an orbit shaker for a few days to ensure complete solvation of the polymer and homogeneity of the solution. The solution was then spin cast onto

circular glass coverslips (1 mm thick, 12 mm diameter) at a rate of 3000 rpm for 30 seconds, then dried under vacuum (15"Hg) at room temperature for one day. Thin, homogeneous, transparent films were prepared with a thickness of  $200 \pm 10$  nm, as determined using a Tencor P-10 Surface Profilometer (Phoenix, AZ). The fluorescence spectrum of each film was recorded and the films subsequently stored in a dessicator in the absence of light at room temperature.

NO<sub>2</sub> exposure of the films was performed under static conditions using gas tight Pyrex glass vessels. A typical exposure experiment was as follows: one sensor film was placed in a 500 mL vessel which was then evacuated to 50 μmHg and backfilled with nitrogen to atmospheric pressure. The process was repeated twice, evacuated once more then backfilled with a NO<sub>2</sub>/N<sub>2</sub> gas mixture (Matheson Gas Co., Denver, CO). Three gas mixtures of 10 ppm, 100 ppm, and 1000 ppm NO<sub>2</sub>/N<sub>2</sub> were used in this investigation.

Fluorescence spectra of the films prior to and after NO<sub>2</sub> exposure were recorded on a SPEX Fluoromax II Spectrophotometer (Edison, NJ), infrared (IR) spectra recorded on a Perkin-Elmer 1750 Infrared Fourier Transform Spectrometer (Norwalk, CT), and UV-vis spectra measurements obtained on a Perkin-Elmer Lambda 19 UV/VIS/NIR Spectrophotometer. For fluorescence studies on the PMMA films the excitation wavelength was at 417 nm and emission measured at 442 nm. Bandpasses were set at 5 nm at both excitation and emission with a scan rate of 1 nm/sec.

Nitro-derivatives of perylene were synthetically prepared to compare spectral characteristics with the exposed sensor films. 1- and 3-nitroperylene were prepared by reacting perylene with nitric acid in a hot 25% water/1,4-dioxane mixture for 1 hour, followed by quenching of the reaction in water. The precipitates were collected and the

isomers separated with silica column chromatography (50% CHCl<sub>3</sub>/hexanes, 1-nitroperylene R<sub>f</sub> = 0.18, 3-nitroperylene R<sub>f</sub> = 0.08). <sup>1</sup>H NMR spectral data of both compounds were identical to those reported in the literature [11]. Other supporting spectral data are as follows: 1-Nitroperylene - IR (KBr) 3068, 1526, 1358, 1315, 826 cm<sup>-1</sup>; UV-vis (THF) λ<sub>max</sub> = 469 nm (ε = 12,500). 3-Nitroperylene - IR (KBr) 3082, 1526, 1337, 815, 798 cm<sup>-1</sup>; UV-vis (THF) λ<sub>max</sub> = 474 nm (ε = 14,900).

## Results and Discussion

Several polymers were evaluated as supporting matrices for the dye imbibed sensor films. These were polystyrene, polyethylene glycol (PEG), ethylcellulose, polydimethylsiloxane (PDMS), and polymethylmethacrylate (PMMA). The films prepared with PMMA gave the best overall properties and performance. The fluorescence emission of a thin PMMA film imbibed with perylene dye is shown in Figure 1, as spectrum A. The spectral characteristics were nearly identical to that of perylene in toluene solution at 0.1 μM concentration. Under identical film preparation conditions (spin cast from chlorobenzene solution) and film thickness (200 nm), films prepared with PEG and ethylcellulose yielded fluorescence intensities only 10 – 20% that of the PMMA films. These films also produced some excimer emission (λ<sub>max</sub> = 550 nm) indicating phase separation of perylene from the matrix. Films produced with PDMS did not produce any excimer emission but gave about 20% lower fluorescence intensity compared to the PMMA film. Films prepared with polystyrene, on the other hand, produced comparable fluorescence to the PMMA films, but gave poor optical response to



NO<sub>2</sub>. Losses in fluorescence intensity and excimer formation in the former polymer films appear to indicate poor solvation of the non-polar perylene in polar matrices.

The solvent used for spin casting was also influential on the spectral and visual characteristics of the films. Films were prepared from solutions of tetrahydrofuran (THF), benzene, toluene, chloroform, 1,4-dioxane, and chlorobenzene. The oxygen containing solvents, THF and 1,3-dioxane, produced films that were slightly opaque with significantly reduced perylene fluorescence, even after extensive drying. UV-vis spectral analyses of these films found identical perylene concentrations to those prepared from chlorobenzene that gave strong fluorescence. Films prepared from chloroform solution were not reproducible in film thickness. Among the remaining solvents, films produced with chlorobenzene yielded the highest reproducibility and optimal spectral properties with the PMMA films.

NO<sub>2</sub> exposure to the perylene/PMMA film induced a decrease in the overall spectral intensity of the fluorescence emission. Figure 1 shows the fluorescence spectra of a film prior to (A) and after (B) exposure to 1000 ppm NO<sub>2</sub> for 1 hour at room temperature. The response is irreversible and selective for NO<sub>2</sub>. Exposure to SO<sub>2</sub>, CO, Cl<sub>2</sub>, and NH<sub>3</sub> at concentrations up to 1000 ppm in a nitrogen atmosphere produced no fluorescence changes even after exposures of over 10 days. The films were also stable in air yielding no detectable optical changes in the film upon storage in the dark over a six-month period.

**Insert Figure 1**

The fluorescence quenching observed with these films upon NO<sub>2</sub> exposure is believed to be due to an irreversible reaction with perylene to produce non-fluorescent nitroperylene adducts (Figure 2) [12,13]. Nitration products of perylene in the exposed films were identified through IR, UV-vis, and fluorescence spectroscopies. The dark red powders of 1- and 3-nitroperylene were prepared and isolated for use as a comparison with the exposed films. Films exposed to the higher concentrations of NO<sub>2</sub> over extended periods of time became reddish in color. Infrared spectra of these films exhibited absorptions at 1526 and 1340 cm<sup>-1</sup>, indicative of the -NO<sub>2</sub> asymmetric and symmetric stretch, respectively, for both 1- and 3-nitroperylene [12]. No absorptions at these wavenumbers are observed in the film prior to exposure. The UV-vis spectra of exposed films yielded absorptions at 470 nm confirming the presence of the nitroperylene isomers. Figure 3 shows UV-vis spectra of a film prior to (A) and after (B) exposure to 1000 ppm NO<sub>2</sub>/N<sub>2</sub> gas for 4 hours.

Insert **Figure 2**

Insert **Figure 3**

Both nitroperylene isomers have relatively little fluorescent properties compared to perylene. Whether dissolved in THF solvent (1.0 μM) or imbibed in the PMMA films, 1-nitroperylene was non-fluorescent at all wavelengths of excitation. In THF solution, 3-nitroperylene did yield a weak emission at 565 nm upon excitation at 474 nm. However, at the excitation wavelength of 417 nm, the fluorescence of either nitroperylene isomer was insignificant in comparison to the emission of perylene.

Fluorescence quenching of the perylene dye showed a rate dependence on the concentration of NO<sub>2</sub> in the atmosphere. Plots of the emission intensity at 442 nm vs. time produced response curves from exposures of 10, 100, and 1000 ppm NO<sub>2</sub>/N<sub>2</sub> atmospheres (Figure 4). Due to the irreversibility of the optical response complete fluorescence quenching should be achieved at all concentration levels. At the highest concentration of 1000 ppm NO<sub>2</sub> this was readily observed within the experimental time frame. At the lower concentrations the response did not reach complete quenching over the course of two-week experiments.

Bartlett and Gardner recently analyzed the situation of coupled diffusion and nonlinear chemical reaction within homogeneous thin films [14]. Assuming the local chemical reaction can be described by second order kinetics, the concentration  $a(x,t)$  of the diffusing species is described by the following equation,

$$D \frac{\partial^2 a}{\partial x^2} - k_f a(1 - \theta)N + k_b \theta N = \frac{\partial a}{\partial t} \quad \text{Equation 1}$$

Where  $\theta$  is the fraction of occupied sites,  $N$  is the concentration of binding sites,  $D$  the diffusivity, and  $k_f$  and  $k_b$  are the forward and backward binding or reaction constants. While this equation does not have an exact analytical solution, the authors identified several limiting cases where approximate expressions for the concentration profiles are accurate. By using a dimensionless analysis the response data could be fit to curves generated from Equation 1. In the situation where the kinetics of the reaction/adsorption is slow relative to diffusion of the adsorbate, an analytical expression for the solution is,

$$\theta(x, \tau) \approx 1 - \exp(-\lambda \gamma \kappa \tau / \eta) \quad \text{Equation 2}$$

where  $\theta$  is still the fraction of occupied sites,  $\chi$  and  $\tau$  are the dimensionless distance ( $x/L$ ) and time ( $Dt/L^2$ ),  $\lambda = Ka_{\infty}$  ( $a_{\infty}$  is the species concentration at infinite distance from the surface and  $K$  is the equilibrium reaction constant,  $k_f/k_b$ );  $\gamma = a/a_{\infty}$ ;  $\kappa = k_fNL^2/D$ ; and  $\eta = KN$ . This equation simplifies to  $1 - \exp(-\kappa a_{\infty} t)$ , hence a plot of  $\theta$  vs  $t$  as shown in Figure 4 fits nicely with the experimental data. The fraction of unoccupied sites was derived by computing the  $\theta$  over the entire thickness of the film and then integrating the result, which then gives the  $\theta$  from Equation 2 as a function of time. Subtracting this value from 1 allows comparison with the experimental results shown in Figure 4.

Based on the fit of Equation 2 with the experimental data, we feel that the assumptions made are reasonably accurate and that there is no kinetic barrier at the film surface, the binding is in accord to a Langmuir isotherm, there are non-linear kinetics, and the film is saturated at equilibrium. The most important conclusion is that there are slow reaction kinetics compared to diffusion and the forward reaction constant fit to experimental data  $k_f \sim 0.06 \text{ (ppm}\cdot\text{min)}^{-1}$  for the particular material tested. Improving the sensor reported on here will require more sites or a faster reaction constant, which may affect diffusion and change conditions for performance.

The model above allows a facile determination of atmospheric concentration of  $\text{NO}_2$  using the sensor material's rate of response. For conditions where a constant concentration of  $\text{NO}_2$  is being sampled an accurate measurement can now be attained. In applications where the  $\text{NO}_2$  concentration continuously evolves, as in HE material degradation, modifications to the model can be made to quantify  $\text{NO}_2$  concentrations at

specific time intervals. We are currently addressing this issue and will describe these efforts in forthcoming publications.

#### **4. Conclusions**

Thin films of perylene doped PMMA provide robust and selective optical sensor materials for the detection of NO<sub>2</sub> in the gas phase. The materials are easily prepared, inexpensive, and offer long shelf life at ambient conditions. These materials also can be readily configured to existing off-the-shelf optical hardware (i.e., LED excitation sources, compact CCD spectrometers) for remote sensing applications. Fluorescence quenching of the sensor films upon exposure to NO<sub>2</sub> was determined to be caused by the formation of nitroperylene. The observed fluorescence response vs. time data could be described using a dimensionless analysis involving coupled diffusion with a nonlinear chemical reaction. Through this theoretical approach NO<sub>2</sub> concentrations in mixed gas systems can be determined.

#### **Acknowledgements**

We would like to thank Dr. William Andrzejewski for his helpful discussions regarding HE material degradation. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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## **Biographies**

*Jimmy D. Cox* graduated from the University of New Mexico in 1999, with a B.S. in Biochemistry. His present research focuses on the biocompatibility of thin organic films in the context of microdevices.

*Phillip I. Pohl* has degrees in Chemical Engineering from the University of New Mexico (Ph.D. - 1996, B.S.-1986) and the University of Texas at Austin (M.S. -1988). He worked as a Research Engineer at Pacific Northwest Laboratory over 4 years before joining the Sandia National Laboratories. His expertise is in applying molecular modeling and contaminant fate and transport theory to remediate hazardous waste sites and to better understand structure-property relationships in natural and man-made materials. He has published over 40 journal articles and reports, and is presently a Principle Member of the Technical Staff.

*Darryl Y. Sasaki* obtained his B.S. at the University of Hawaii, Manoa, in 1984, and Ph.D. in Organic Chemistry at the University of California, Irvine, in 1989. After brief research appointments with ERATO in Kurume, Japan (1989 – 1992), and at the California Institute of Technology (1992 – 1994), he joined Sandia National Laboratories in 1994. He is currently a Principal Member of Technical Staff with research interests in optical sensor materials, self-assembling structures, and molecular recognition.

*Seema Singh* graduated from the University of New Mexico in 1995, obtaining her Ph.D. in Physical Chemistry.



## Figure Captions

Figure 1. Fluorescence emission spectra of a perylene/PMMA film excited at 417 nm before (A) and after (B) a one hour exposure to 1000 ppm NO<sub>2</sub> in nitrogen at room temperature.

Figure 2. Formation of mononitrated adducts of perylene upon NO<sub>2</sub> exposure.

Figure 3. UV-vis spectra of a perylene/PMMA film before (A) and after (B) a four hour exposure to 1000 ppm NO<sub>2</sub> in nitrogen at room temperature.

Figure 4. Fluorescence response vs. time data of the sensor films exposed to 10 ppm (●), 100 ppm (■), and 1000 ppm (▲) NO<sub>2</sub>/nitrogen atmosphere. Theoretical curves derived from Equation 2 are plot as solid lines.

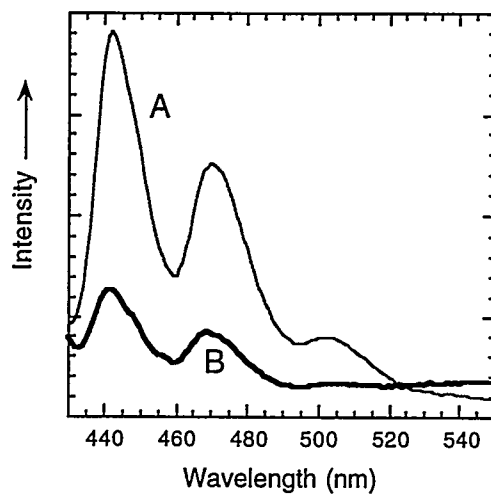


Figure 1

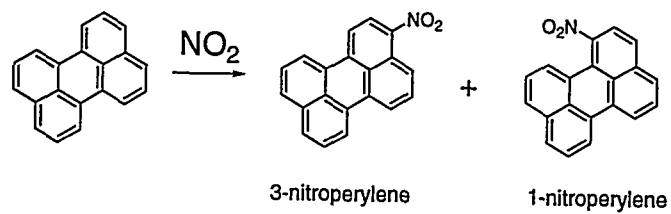


Figure 2

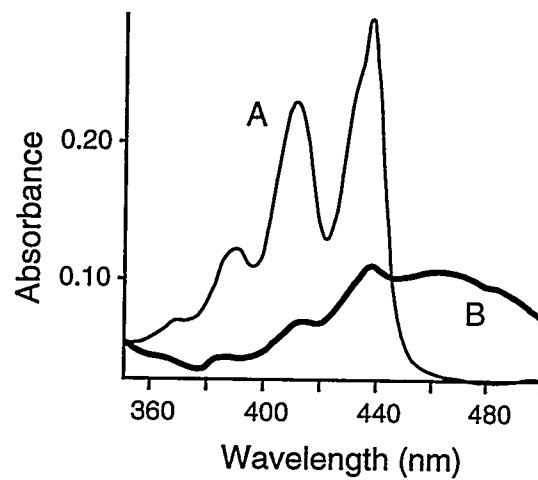


Figure 3

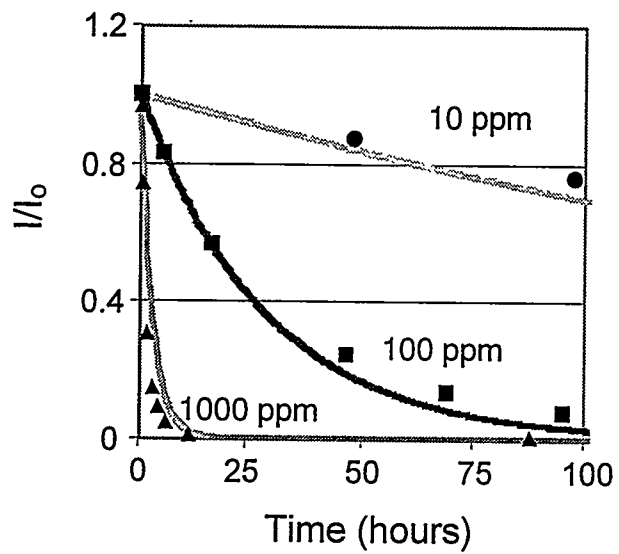


Figure 4