



Assessing the sensing limits of fluorescent dendrimer thin films for the detection of explosive vapors



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ABSTRACT

Photoluminescence quenching of organic thin films is a promising technique for the detection of vapors from explosives. The photoluminescence quenching response depends on the energetics of electron transfer from the photo-excited sensing material to the analytes, the vapor pressure of the analyte, and the diffusion process of the analytes in the sensing films. It is critical that the performance of a potential sensing material be evaluated in the solid-state with a range of analytes and across a range of vapor concentrations to ensure high sensitivities through non-contact sampling are achievable. We have investigated the photoluminescence quenching of three generations of carbazole-based dendrimers across a range of nitro-containing analyte vapor concentrations, including the TNT by-product 2,4-dinitrotoluene (DNT), and the tagging agent 2,3-dimethyl-2,3-dinitrobutane (DMNB). We show that the performance of all three dendrimer generations in the solid-state is near identical. Furthermore, we show that these dendrimers have a high affinity towards nitroaromatic compounds with parts per billion sensitivity, which makes them ideal for trace-level detection.

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1. Introduction

The capability to detect explosives at very low concentrations is essential for the provision of security but also for the remediation of minefields left from past conflicts. While there are a number of technological solutions available, many of which are based on standard analytical chemistry techniques such as mass spectrometry and gas chromatography, they tend to employ bulky, complex devices that are unsuitable for field use. Cheaper and more portable solutions are often based on colorimetric detector kits, but these require the user to collect a sample from the suspicious object in order to generate a reliable response, therefore placing the user in danger. One promising technology for the standoff detection of explosive vapors is by photoluminescence (PL) quenching, where the relative simplicity of the technology needed to generate and measure the luminescent signal means that detectors can be very compact, battery powered and rugged.

At a fundamental level the sensing material needs to be luminescent in the solid-state [1–5] with the energy of the excited electron in the S_1 state sufficiently higher than the electron affinity of the analyte to overcome the exciton binding energy and enable electron transfer between the fluorophore and the analyte. This process is often described in terms of the relative energies of the lowest unoccupied molecular orbital (LUMO) of the sensing material and analyte [6,7]. The sensing of analytes using PL quenching is a straightforward process. In the absence of an analyte, photo-excitation of the fluorescent sensor leads to an exciton that can decay radiatively. However, in the presence of an analyte molecule, the photo-excited electron of the exciton can transfer to the analyte and form a “charge transfer” state. This state relaxes non-radiatively to the ground state by back-electron transfer and, hence, the PL of the sensing material is quenched.

There is an extensive body of published literature on PL quenching studies of potential sensing materials by nitrated analytes, but most of these were performed in solution [1,3,4,8,9]. However, the relevance of solution-based characterization towards solid-state detection is questionable [10], given that the manner in which the analytes and chromophores interact with each other is different in the two phases. Considering that any real-world application of this technology will likely be based upon solid-state sensing media, it is therefore essential that the performance of any potential sensing

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material be evaluated in the solid-state with appropriate analytes and at vapor concentrations that are below the level of a saturated atmosphere to reflect the fact that in the real world explosives are likely to be concealed or encased, which will inhibit accumulation of vapors.

We have previously reported a series of three generations of carbazole dendrimers (which we will refer to henceforth as G1, G2 and G3) that display large PL quenching responses to nitroaromatic analogues of the high explosive 2,4,6-trinitrotoluene (TNT) in solution [11]. For each dendrimer generation, four carbazole dendrons were attached to the spirobifluorene core, which leads to macromolecules with a more three-dimensional shape. It was observed that the Stern-Volmer constants with 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) approximately doubled in magnitude between G1 and G2 and then remained the same for G3 [11]. These differences were caused by a change in the location of the chromophore between G1 and the higher generations. In this work we investigate the PL quenching of these dendrimers in the solid-state, and the impact of dendrimer generation on the PL quenching efficiency and recovery with respect to the vapors of DNT, 4-nitrotoluene (pNT) and DMNB over a range of vapor concentrations and exposure times. Furthermore, to understand how the vapors of DNT interact with and are distributed within the dendrimer films we performed a combination of neutron reflectometry with *in situ* PL measurements. We show that despite the significant differences in solution all three dendrimer generations perform similarly in the solid-state although the responses between the analytes themselves are different. We find that ~40 nm thick films exhibit saturated responses to DNT within 10 s even at concentrations as low as 4 ppb with the vapors able to diffuse throughout the film.

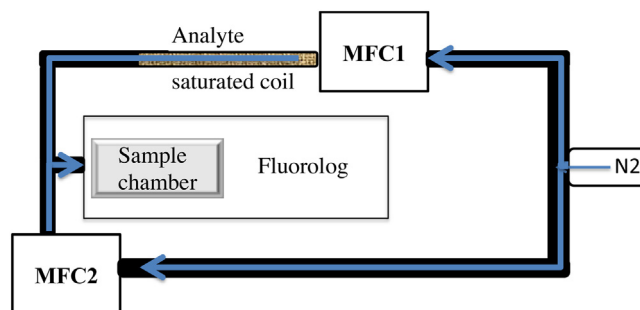
2. Experimental

2.1. Sample preparation

The synthesis of the dendrimers has been previously reported [11]. Thin films of G1, G2 and G3 on fused silica substrates were formed by spin-coating from toluene solutions at a concentration of 10 mg mL⁻¹ at a speed of 2000 rpm. The substrates were rinsed with acetone and 2-propanol prior to spin-coating. The toluene was distilled by rotary evaporation, prior to use. Film thicknesses were in the range of 35–40 nm based on linear extraction of absorption measurements and thickness measurements using a Dektak 150 (Veeco).

2.2. Steady state spectroscopy

UV-visible absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. PL spectra were recorded on a Horiba Jobin-Yvon Fluorolog 3 fluorimeter with an excitation wavelength of 320 nm. Quenching response measurements were carried out on fused silica substrates. The samples were clamped in a custom-built sample holder (Scheme 1) in the fluorimeter. The analyte vapor was introduced into the chamber in a controlled manner by running nitrogen through a coiled section of quarter inch diameter stainless steel tubing coated on the inside with analyte. The vapor concentration delivered by the coil was calibrated by bubbling known volumes of the nitrogen stream at different flow rates through acetonitrile and determining the concentration of the dissolved analyte. To ensure all the analyte vapor was captured by the acetonitrile, three bubblers were used in series. The flow rate and hence concentration of analyte was controlled using a mass flow controller (MFC1). The output from MFC 1 was mixed with that of a second mass flow controller (MFC2) with the resulting flow



Scheme 1. Schematic diagram of the photoluminescence quenching experimental setup.

directed face-on towards the film of the sensing material. Disabling the output of MFC1 resulted in a flow of nitrogen over the sensing material film for the “recovery” experiments. Measurements were repeated 5 times and the absorbance and PL from before and after the (analyte exposed) quenching experiments was also collected to assess the level of photodegradation.

Thin film photoluminescence quantum yield (PLQY) measurements were performed using the procedure described by Greenham et al. [12] Thin film samples were photoexcited using the 325 nm output of a HeCd laser in a nitrogen-purged integrating sphere. Unless otherwise stated, the excitation wavelength used for the PL measurements was 320 nm.

2.3. Neutron reflectometry

Neutron reflectometry was performed using the Platypus time-of-flight neutron reflectometer and a cold neutron spectrum ($2.8 \text{ \AA} < \lambda < 18.0 \text{ \AA}$) at the OPAL 20 MW research reactor [Australian Nuclear Science and Technology Organisation (ANSTO), Sydney, Australia] [13]. Neutron pulses of 23 Hz were generated using a disk chopper system (EADS Astrium GmbH) in the medium resolution mode ($\Delta\lambda/\lambda = 4\%$) and recorded on a 2-dimensional helium-3 neutron detector (Denex GmbH). Reflected beam spectra were collected at 0.5° for 1 h (0.4 mm slits) and 2.0° for 4 h (1.6 mm slits). Direct beam measurements were collected under the same collimation conditions for 1 and 3 h (with attenuator) for each respective slit size. *In situ* PL spectra of the films were simultaneously measured with an Ocean Optics USB2000 spectrometer exciting with a 365 nm Nichia UV-LED. For the neutron reflectometry measurements, films of G1, G2 and G3 were spin-coated onto 2 in. silicon wafers (Si-Mat, Germany) from solutions with concentrations of 25 mg mL⁻¹ in toluene at 2000 rpm to give films of thickness in the range of 85–90 nm. Glass jars containing approximately 50 mg of per-deuterated DNT (prepared by dinitration of d8-toluene) covered with cotton wool were left to equilibrate overnight. For saturated film measurements the films of the dendrimers were placed in the jars for approximately 5 h at room temperature, which ensured equilibrium between the analyte vapors and analyte in the films was reached. A small amount of solid analyte was also placed in the neutron sample chamber in order to maintain equilibrium throughout the neutron reflectivity measurement. To remove the d-DNT vapors from the film and recover the PL the films were placed in a stream of clean, dry air for 5 min. Analysis of the reflectivity profiles was performed using the Motofit reflectometry analysis program [14]. All models include a 0.8–1.5 nm silicon oxide layer on the surface of the substrate. Interfacial roughness values for the organic layers were all between 0.5 and 1.2 nm and showed little change upon exposure to and removal of the d-DNT vapors. The quoted uncertainties were calculated from the statistical uncertainties based upon the quality of the fit to the measured data.

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