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Diffusion of nitroaromatic vapours into fluorescent dendrimer films for explosives detection

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ABSTRACT

Fluorescence-based sensing with organic semiconductors is a powerful method for the detection of a broad range of analytes including explosives, chemical weapons and drugs. Diffusion of an analyte into an organic semiconductor thin film, and its subsequent interaction with the chromophore are key factors that govern the sensing performance of a chemosensor. In this study the diffusion behaviour of an explosive analyte analogue into a sensing film of a conjugated dendrimer was investigated using a quartz crystal microbalance (QCM) and correlated with neutron reflectivity measurements. The mechanistic insights of *para*-nitrotoluene (*p*NT) sorption in the films of different thicknesses of a first generation dendrimer with fluorenyl surface groups, carbazole dendrons and a spirobifluorene core were studied and interpreted in terms of the underlying kinetics and thermodynamics. Sorption measurements suggest that the process of diffusion of *p*NT vapour into the dendrimer films is Super Case II, which involves swelling of the film. Swelling of the film was confirmed by neutron reflectometry, which also showed uniform distribution of the *p*NT molecules throughout the film. The activation energy barrier and change in Gibbs free energy in the sorption process were calculated from the QCM responses. The sorption process was found to be thermodynamically (not kinetically) controlled and independent of film thickness. This work sheds insight into the structure–property relationships that govern the performance of organic semiconductor fluorescence-based chemosensors.

1. Introduction

Due to the reality of terrorist threats and security issues across the globe, the development of rapid and reliable detection of military explosives at a stand-off distance is an important scientific and technological challenge [1]. The development of fluorescence quenching-based chemical sensors offers a route towards portable and compact devices [2–4]. Such sensors have been successfully incorporated in a lightweight, portable system, which is now commercially available under the brand name Fido (FLIR Systems, Inc.) [5,6]. However, issues such as selectivity, sensitivity, and reversibility are always critical considerations. Hence, understanding how the analyte molecules diffuse into the sensing films and interact with the chromophore is an important endeavour.

The fluorescence quenching process used in chemical sensing is relatively straightforward: the electron from a photogenerated exciton on the fluorescent sensing compound is transferred to the analyte and relaxes non-radiatively back to the ground state, resulting in a loss of fluorescence [4,7]. For this mechanism to function it is therefore essential that the energy of the excited electron on the fluorescent compound is higher than the electron affinity of the analyte with the difference in energy sufficient to enable electron transfer and exciton dissociation [7]. However, beyond the electronic requirements it is also important that the sensing material possesses a chemical or physical affinity for the analyte and is sterically compatible. Hence, the way in which the analyte molecules diffuse into the sensing film and interact with the fluorophore are of particular relevance for solid-state sensors.

Conjugated polymers have been widely studied as fluorescent sensing materials [8–10], and indeed the active material in Fido is believed to be a conjugated polymer [11]. More recently, fluorescent dendrimers have shown substantial potential as explosive sensing materials [12–18] owing to their high photoluminescence quantum yields, monodispersity and the ability to control and tailor the physical properties through tuning of the chemical structure.

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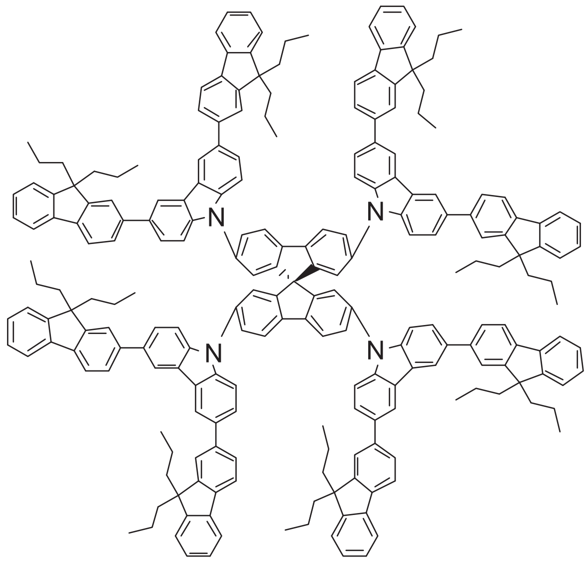

Fig. 1. Chemical structure of the first generation sensing dendrimer based on a 9,9′-spirobifluorene core with carbazole dendrons and 9,9-di-*n*-propylfluorene surface groups.

We have previously reported that neutron reflectometry can be used to measure the difference in film composition between a neat dendrimer film and when it is saturated with an analyte. However, while neutron reflectometry can be used to follow the analyte desorption for a thermally activated process it does not have the sensitivity or time resolution to measure the sorption of the analyte, which is when the initial response of the sensor is triggered [14,18]. In this study, we have utilised a custom-built experimental setup enabling time-resolved quartz crystal microbalance (QCM) measurements to monitor the analyte uptake in dendrimer sensing films, thus providing important information about the diffusion behaviour for such materials. QCM was chosen for the study, as mass changes at the nanogram level are quantifiable [19,20]. The sensitivity of QCM also means it is potentially a sensing platform for the detection of explosives [21–23].

The model analyte used was an analogue of the high explosive 2,4,6-trinitrotoluene (TNT), *para*-nitrotoluene (*p*NT). It was chosen due to it possessing a higher vapour pressure (200 ppm) [24] than TNT (10 ppb) [16] as well as being safer to use. The sensing film was a layer of a first-generation dendrimer comprised of a 9,9′-spirobifluorene core, carbazole dendrons and 9,9-di-*n*-propylfluorene surface groups (Fig. 1) [13,14]. This sensing material was chosen because of its high affinity for nitroaromatic vapours, which are known to rapidly quench the fluorescence of thin films [14]. As mentioned above, QCM measurements were used to quantify the analyte uptake (sorption) with the results correlated with neutron reflectometry. The QCM responses enable us to quantify sorption rate, diffusion coefficient and mole ratio of analyte to dendrimer. Thermodynamic properties of the diffusion process, such as activation energy and Gibbs free energy were also evaluated from the QCM responses. The present article thus describes in detail the sorption behaviour of *p*NT molecules into films of a dendrimer.

2. Experiment

2.1. Instrumentation

Fig. 2 shows a schematic diagram of the custom-built experimental setup for the QCM experiments, all of which were undertaken at an ambient temperature of 22.5 ± 1.0 °C. The chamber, comprising a QCM holder and gas-mixing compartment, is semi-airtight and is supplied by mass flow controllers controlling the flow rates of the carrier gas (nitrogen). One line enters directly into the gas-mixing compartment (nitrogen only) with the second line passing through a *p*NT-coated coil to introduce the analyte vapour. Mixing of the gas streams is aided by the baffles in the mixing chamber, which also minimise disturbance of the QCM by the gas stream. The QCM chip was sandwiched between two O-rings within a Teflon holder, which secure its position and reduce vibration and drift. The diameters of the quartz crystal and gold electrode were 13.7 and 5.11 mm respectively. The CH Instruments Model 400B utilises a time-resolved mode to measure the frequency difference between the working crystal (7.990–7.955 MHz) and the reference crystal oscillations (8.000 MHz). The Sauerbrey equation was used to estimate the mass changes (ΔM) from the frequency changes (ΔF) of the crystal output given by [25]

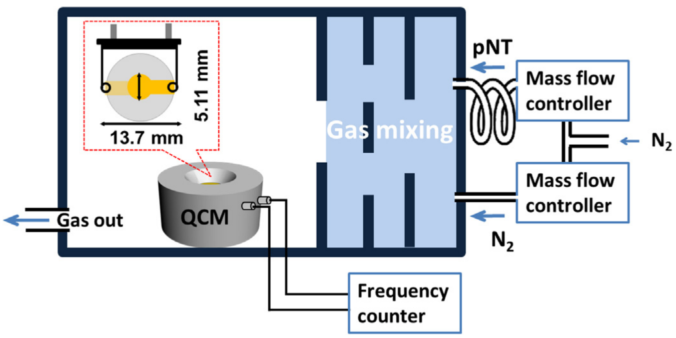

Fig. 2. Schematic of the custom-built experimental setup with the dimensions of the quartz crystal microbalance (QCM) chip shown in the inset.

$$\Delta F = \frac{-2f_0^2}{A(\mu\rho_c)^{1/2}}\Delta M, \tag{1}$$

where f_0 is the resonant frequency of the fundamental mode of the crystal, A is the area of the gold disc coated onto the crystal (0.205 cm^2), ρ_c is the density of the crystal and μ is the shear modulus of quartz. The density of the crystal was 2.648 g/cm^3 and the shear modulus was 2.947×10^{11} g/cm s^2 (data provided by CH Instruments, Inc.). Therefore, for an 8 MHz crystal, a 0.1 Hz change in frequency corresponds to a mass change of 0.14 ng. However, it is important to note that QCMs are very sensitive to the environment including local vibrations and temperature changes. We therefore measured the QCM drift under nitrogen at a flow rate of 1500 mL/min and found that the frequency varied by up to ±5 Hz during a 6000 s running time, which corresponds to an uncertainty of ±7 ng in the measurements. It is important to note that this uncertainty in the mass is greater than the differences observed in separate measurements under the same conditions, and hence sets the upper limits on the errors. Each sorption experiment was repeated three times and average values taken for further calculation.

2.2. Coating the QCM electrode

An Xdip-SV1 dip-coater was employed for coating the QCM chip. The QCM chip was first cleaned using toluene, followed by rinsing with ethanol and acetone before being dried with a stream of nitrogen. It was then immersed in a 10 or 15 mg/mL solution of the dendrimer in toluene and withdrawn from the bath at a prescribed withdrawal speed to control the final film thickness. The process was done under ambient conditions. The film was then left to dry in air.