

Molecular versus exciton diffusion in fluorescence-based explosive vapour sensors

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Supplementary Information

Experimental Section:

Materials:

A first-generation dendrimer comprised of a 9,9,9',9'-tetra-*n*-propyl substituted 2,2'-bifluorene core, first generation biphenyl dendrons, and 2-ethylhexyloxy surface groups (D1) and another first-generation dendrimer comprised of a tris(4-(9,9-di-*n*-propyl-9*H*-fluoren-2-yl)phenyl)amine, biphenyl dendrons, and 2-ethylhexyloxy surface groups (D2) (shown in Fig. 1) were chosen as they are known to respond to nitroaromatic vapours. They were synthesised according to the literature.^{1,2} Two chemically similar polymers, poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)]-end capped with 2,4-dimethylphenyl (P1) and poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*co*-(*N,N'*-diphenyl)-*N,N'*-di(*p-n*-butylphenyl)-1,4-diaminobenzene)] end capped with 2,4-dimethylphenyl (P2) were purchased from American Dye Source, Inc. for comparison (structures shown in Fig. 1). The molecular weight of P1 and P2 were 13 kDa (PDI = 3.4) and 114 kDa (PDI = 2.1) respectively.

Instrumentation:

A sealed custom-built experimental setup was used for the diffusion measurements (Supplementary Fig. 1) comprised of a quartz crystal microbalance (QCM) to measure mass changes, a light emitting diode (LED) with 365 nm peak emission as the excitation source, a lens coupled to an optical fibre to collect the PL and transmit it to a CCD spectrograph

(AvaSpec-3648). Two mass flow controllers were used to deliver the carrier gas (nitrogen) directly to the chamber. One line enters directly into the gas-mixing compartment (nitrogen only) while the second line passes through a coil coated on the inside with the analyte to introduce analyte vapour into the gas stream. Mixing of the gas streams was aided by the baffles in the mixing chamber, which also minimise disturbance of the QCM by the gas stream. A CH Instruments Model 400B series instrument, operated in time-resolved mode, was employed to measure the frequency difference between the working crystal (7.990 MHz – 7.955 MHz) and the reference crystal oscillations (8.000 MHz). The mass change (Δm) was derived from the frequency changes (Δf) of the crystal output, according to

$$\Delta f = \frac{-2f_0^2}{A(\mu\rho)^2} \Delta m \quad (1)$$

where f_0 is the resonant frequency of the fundamental mode of the crystal, A is the area of the gold electrode (= 0.205 cm²), ρ (= 2.648 g/cm³) is the density of quartz, and μ (= 2.947×10¹¹ g/cm.s²) is the shear modulus of quartz. The PL signal was integrated over the emission range of 400-550 nm with an integration time of 1 s.

Film deposition on QCM crystals:

The QCM chips were cleaned using toluene, followed by rinsing with acetone and dried with a stream of nitrogen. The films were coated on the QCM chips from 5 to 15 mg/mL toluene solutions by dip-coating (Xdip-SV1) in air. Film thickness was controlled by varying the concentration of the dendrimer solution and the withdrawal speed of the QCM chip from the solution.³ Two independent methods were utilised to measure the film thickness. The first involved determining the film absorption coefficient of a material and then calculating the thickness from the absorbance of the film at two positions on the QCM chip (see Supplementary Fig. 1). To determine the absorption coefficient, the thicknesses of the films were measured with a Veeco Dektak 150 surface profilometer. The second method was to calculate the film thickness on the gold surface using the measured film mass by QCM,³ and assuming a mass density of the film of 1 g cm⁻³. Both methods gave similar thickness values (within 10 % error) with the average used for calculations and analysis. The errors in the

thicknesses were calculated from three films deposited using the same conditions and are thus representative of the level of variability in the film deposition process.

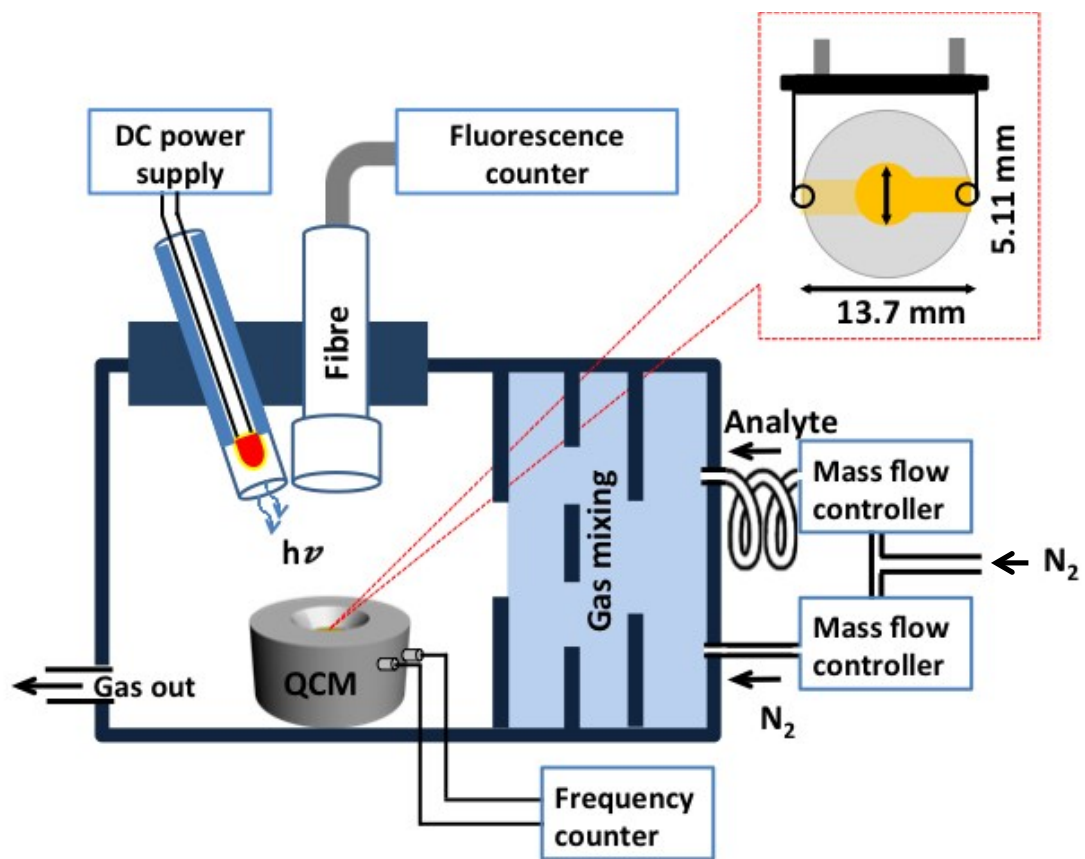
Spectroscopy:

To measure the photophysical properties, films of the sensing materials were prepared from solutions in spectrophotometric grade toluene and spin coated on fused silica substrates. Absorbance spectra were measured by a Varian Cary 5000 UV-Vis-NIR spectrometer and PL spectra were measured with a Horiba Jobin-Yvon Fluoromax 4 fluorometer.

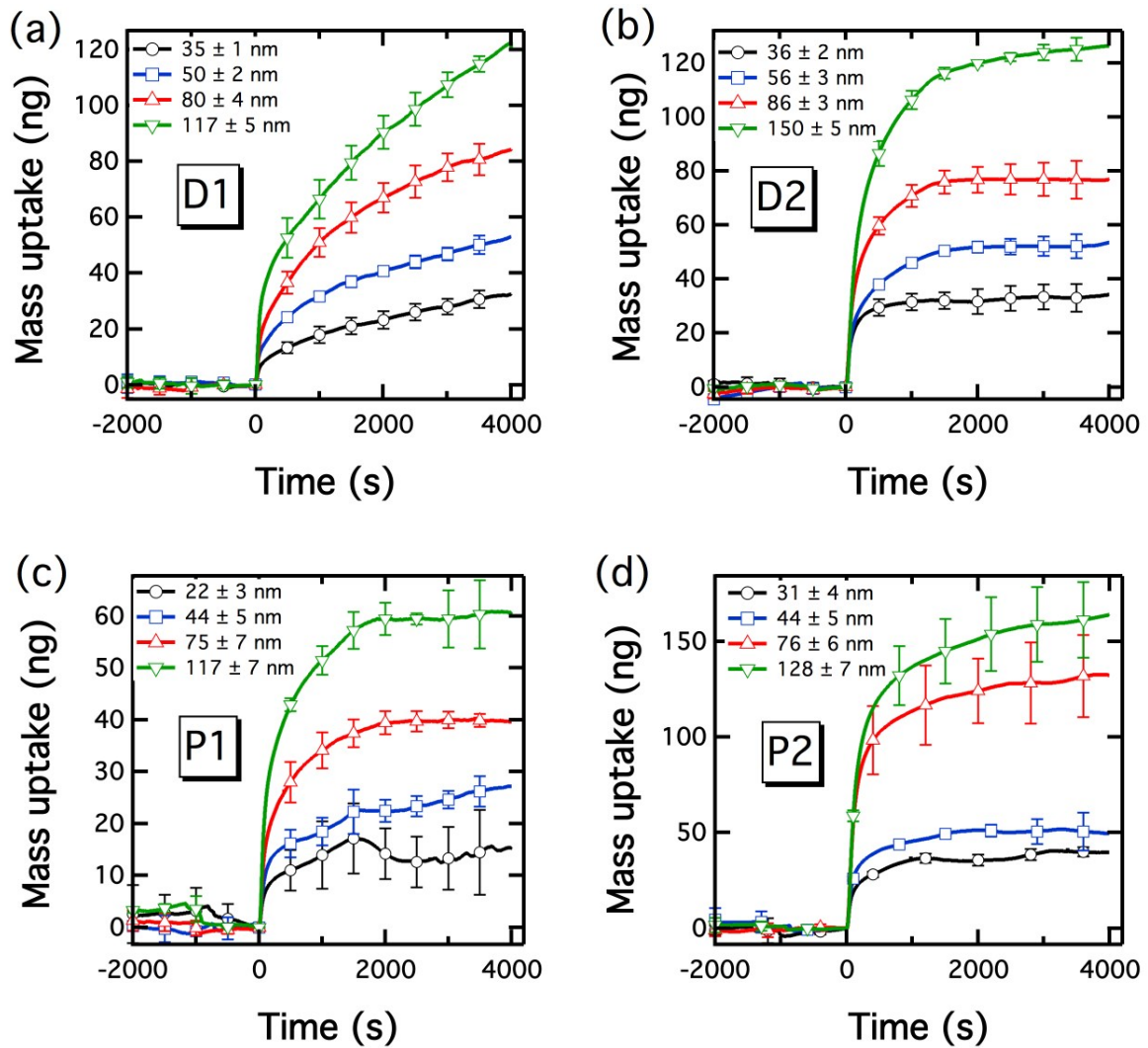
Photoluminescence quantum yield measurement:

The photoluminescence quantum yields (PLQY) were measured using the method reported by Greenham et al.⁴ Spin-coated films were photo-excited with the 325 nm output (power was 200-300 μ W) of a HeCd laser and the emission collected with an integrating sphere. The interior of the sphere was flushed with nitrogen to reduce sample photo-degradation.

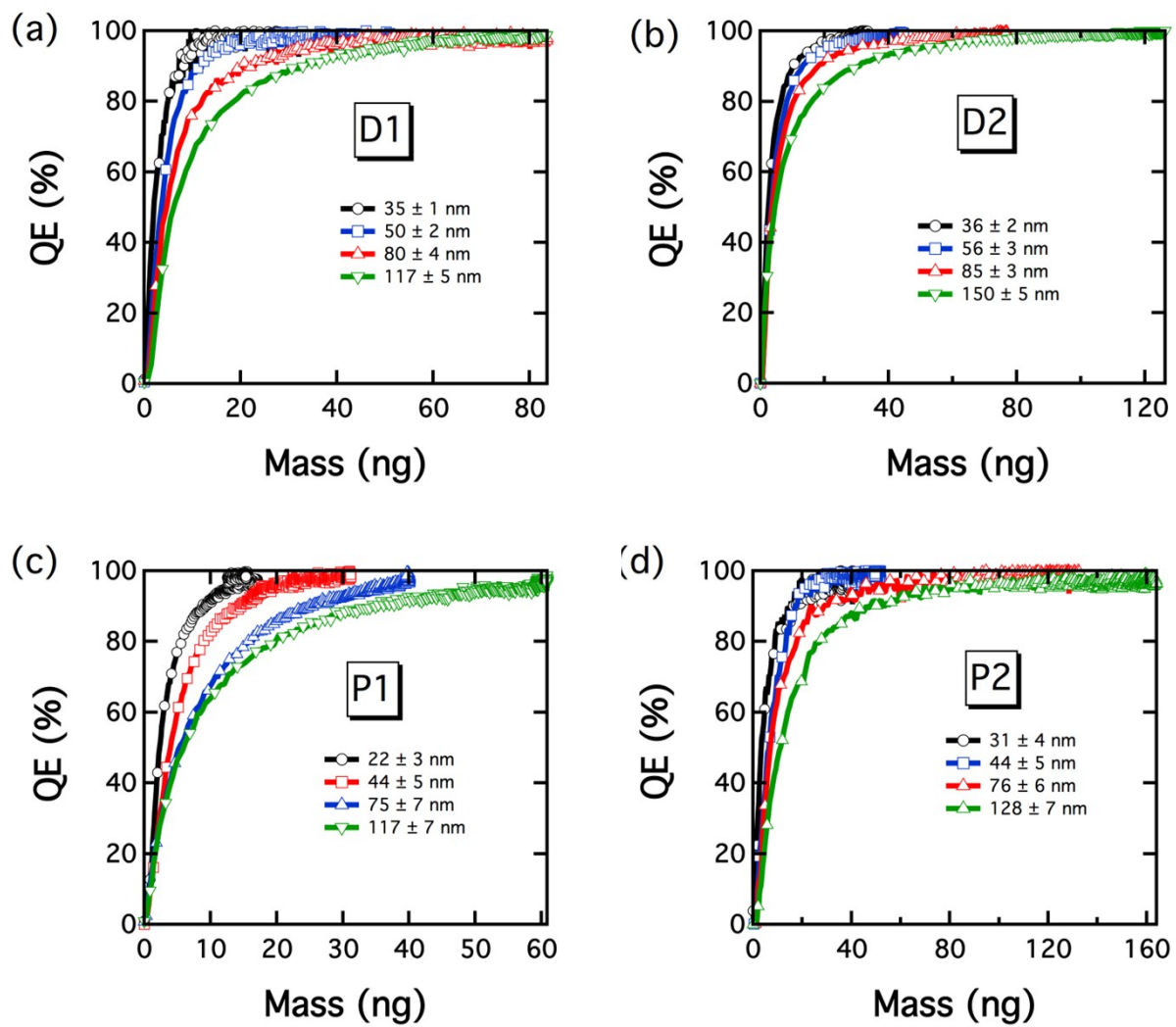
Supplementary Figures:



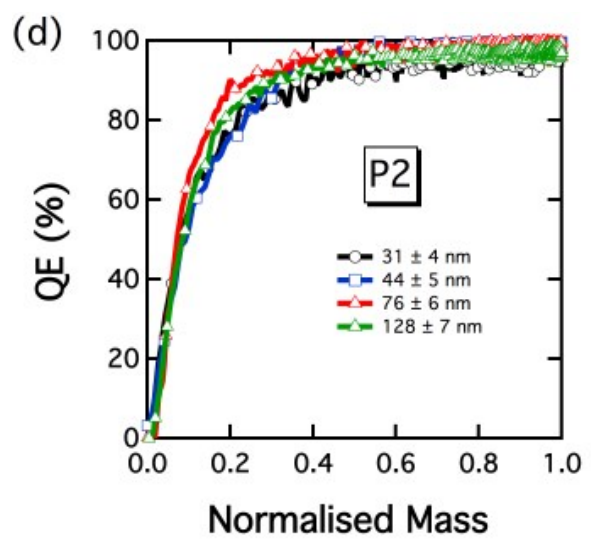
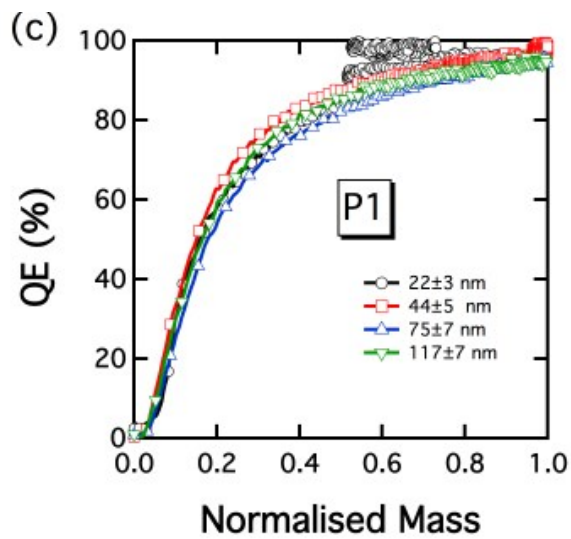
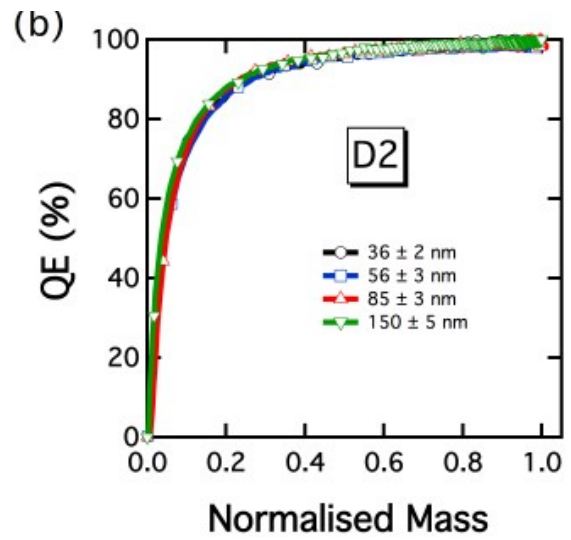
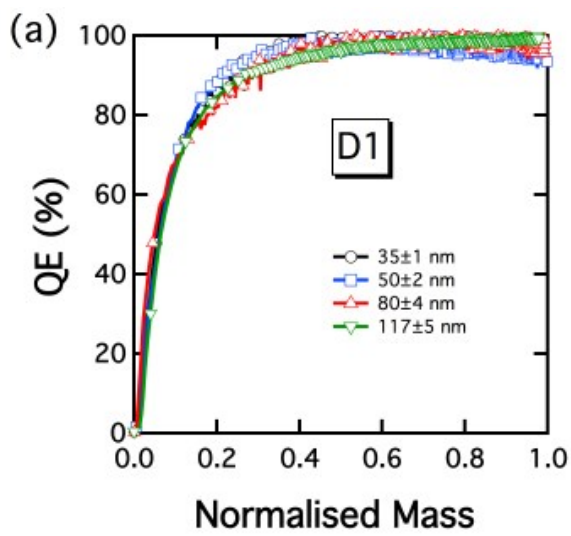
Supplementary Fig. 1. Schematic diagram of the experimental setup.



Supplementary Fig. 2. *p*NT mass uptake for films with a range of thicknesses as sorption proceeds. The errors were calculated from three repeat measurements with the films of similar thicknesses.



Supplementary Fig. 3: Quenching efficiency (QE) as a function of *p*NT mass uptake for films of different thicknesses.



Supplementary Fig. 4: QE versus normalised *p*NT mass uptake for films of different thickness.

Supplementary Table:

Supplementary Table 1: Photophysical properties of the sensing materials in the solid state.

Molecule	Peak absorbance (nm)	Peak emission (nm)	Absorption coefficient at λ_{\max} ($\times 10^5 \text{ cm}^{-1}$)	PLQY (%)
D1	351	393	1.5 ± 0.1	49 ± 5
P1	387	427	2.3 ± 0.1	47 ± 5
D2	373	434	1.2 ± 0.1	35 ± 4
P2	377	459	2.2 ± 0.1	25 ± 3

References:

1. H. Cavaye, P. E. Shaw, X. Wang, P. L. Burn, S. C. Lo and P. Meredith, *Macromolecules*, 2010, **43**, 10253-10261.
2. H. Cavaye, P. E. Shaw, A. R. G. Smith, P. L. Burn, I. R. Gentle, M. James, S. C. Lo and P. Meredith, *J. Phys. Chem. C.*, 2011, **115**, 18366-18371.
3. M. A. Ali, S. S. Y. Chen, H. Cavaye, A. R. G. Smith, P. L. Burn, I. R. Gentle, P. Meredith and P. E. Shaw, *Sensor. Actuat. B: Chem.*, 2015, **210**, 550-557.
4. N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett*, 1995, **241**, 89-96.