Supplementary Material (ESI) for Chemical Communications

Supplemental Information For:

Amplifying Fluorescent Polymer Sensors for the Explosives Taggant 2,3-Dimethyl-2,3-dinitrobutane

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General Methods and Instrumentation. UV/vis spectra were recorded on an Agilent 8453 diode-array spectrophotometer and corrected for background signal with a solvent-filled cuvette. Emission spectra were acquired on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using either right angle detection. Excited state lifetimes were measured using the phase modulation technique and referencing to an aqueous LUDOX scattering suspension.

Materials. All solvents used for photophysical experiments were of spectral grade. 2,3-Dimethyl-2,3-dinitrobutane (DMNB) and benzophenone (BP) were obtained from Aldrich and used without further purification. The preparation and characterization of all polymers investigated in this study has been previously described.[1]

Solution Quenching Experiments. Solution Stern-Volmer experiments were performed via a typical procedure. A stock solution of optically dilute polymer (OD < 0.1 at λ_{max}) in either tetrahydrofuran (THF) or chloroform was prepared. 3.0 mL of this solution was added to a quartz cuvette, while a known amount of the quencher (15-30 mg) was dissolved in an additional 1.0 mL of this polymer stock solution. Aliquots of the quencher/polymer solution were added to the cuvette, and fluorescence spectra of each resulting sample were recorded upon addition of each aliquot under identical instrumental conditions (slit widths, excitation wavelength, etc.). A linear regression of a plot of Φ_0/Φ vs. [quencher] yielded excellent linear fits, the slopes of which correspond to the Stern-Volmer constant (k_{sv}). Dividing k_{sv} by the excited state lifetime of the fluorescent polymer gives the pseudo-first order rate constant for fluorescence quenching (k_q). In all cases, normalization of the first and last emission spectra in each series of quenching experiments showed excellent overlap of the spectra and no generation of new bands due to exciplexes, etc.

[1] See References 3b (**P1**), 6a (**P2, P3, P5-P7**), and 6b (**P4**) from the article text.

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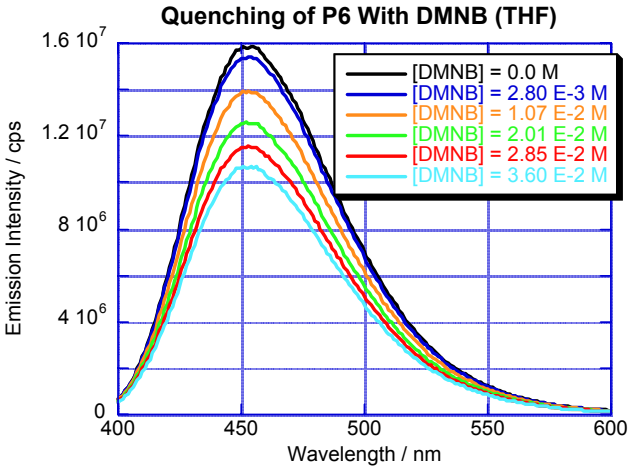
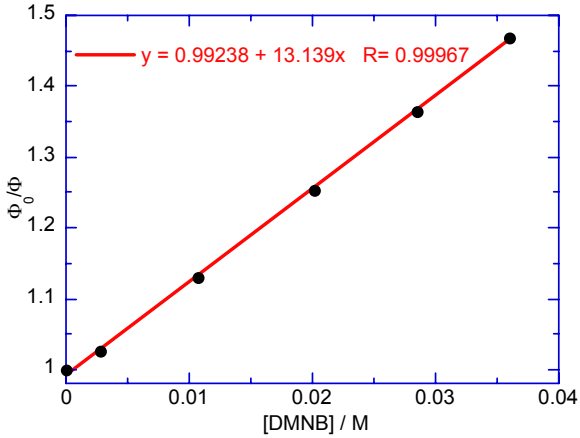
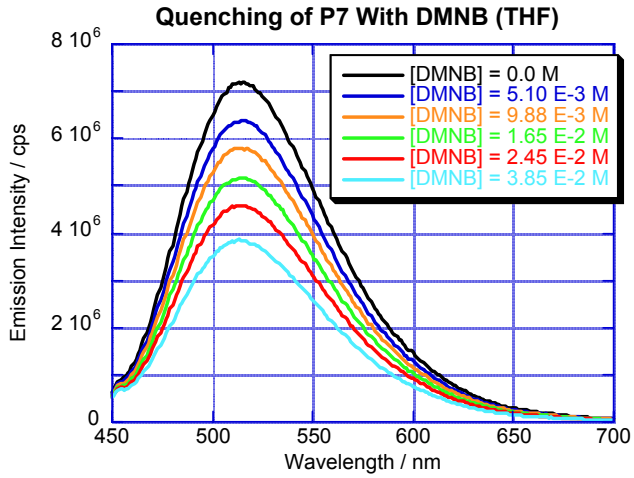
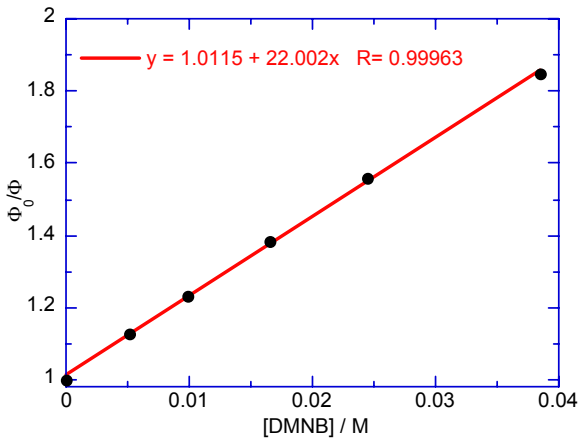
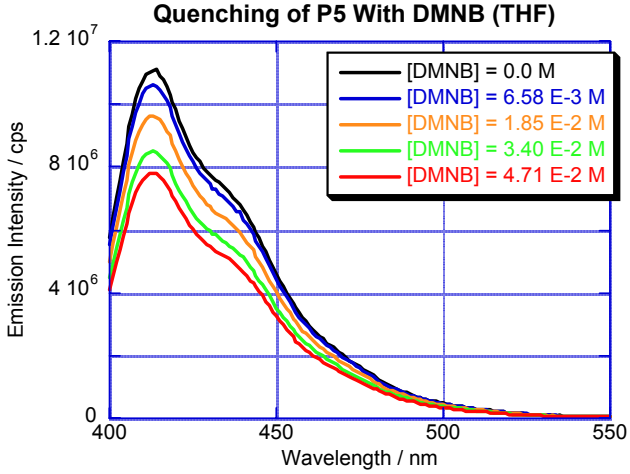
Included below are the results of the Stern-Volmer experiments for polymers which showed readily measured fluorescence quenching by DMNB in solution.

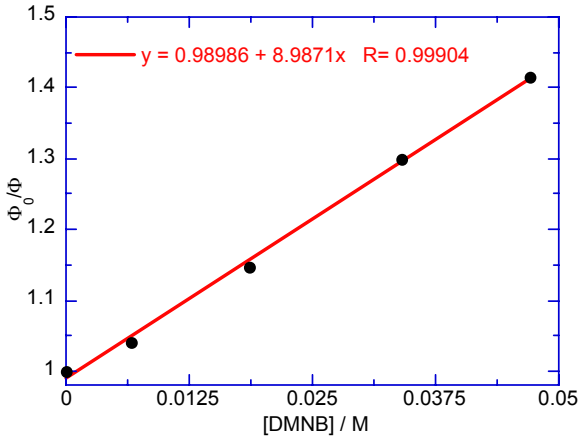


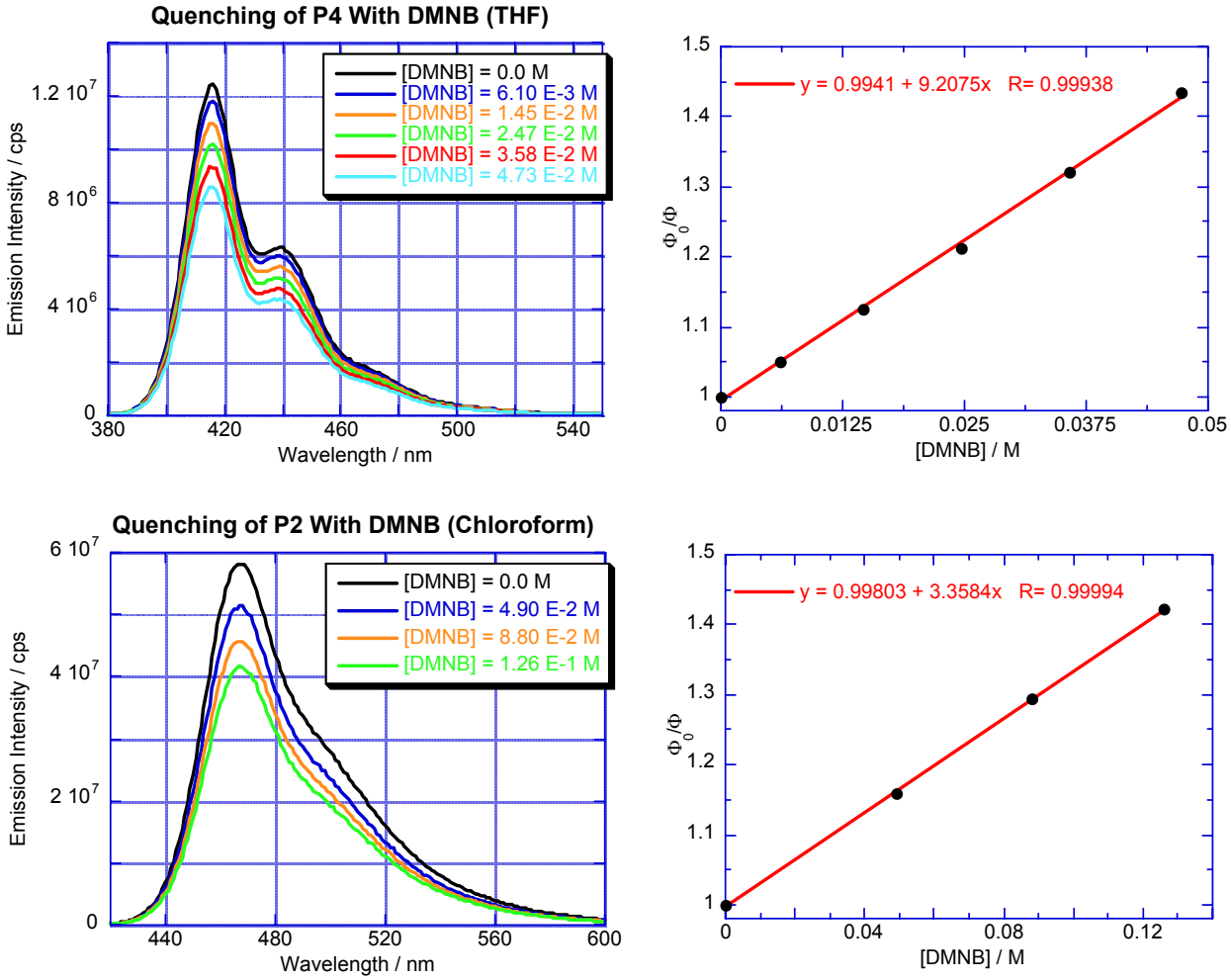












Solid-State Quenching Experiments. Time-dependent solid-state quenching experiments were performed using a Nomadics Fido™ sensor device (www.nomadics.com). A schematic of how this device works is pictured below. The inside of a glass capillary was coated with the conjugated polymer film (spun-cast from a 1 mg/mL solution (THF or $CHCl_3$ at 700 rpm for 1 minute). This capillary was inserted into the sensor, which is equipped with a laser diode (405 nm) and a photodetector. In addition, a pump, operating at 30 cc/min, draws in air from a nozzle through the capillary, exposing the film to an analyte vapor of the users choice (in this work DMNB or benzophenone). The total emission is then continuously monitored. Vapors were introduced by manually holding a vial (20 mL size) that contains some of the analyte solid and a piece of cotton up to the nozzle of the Fido device. Additional solid-state quenching experimental data is shown below.

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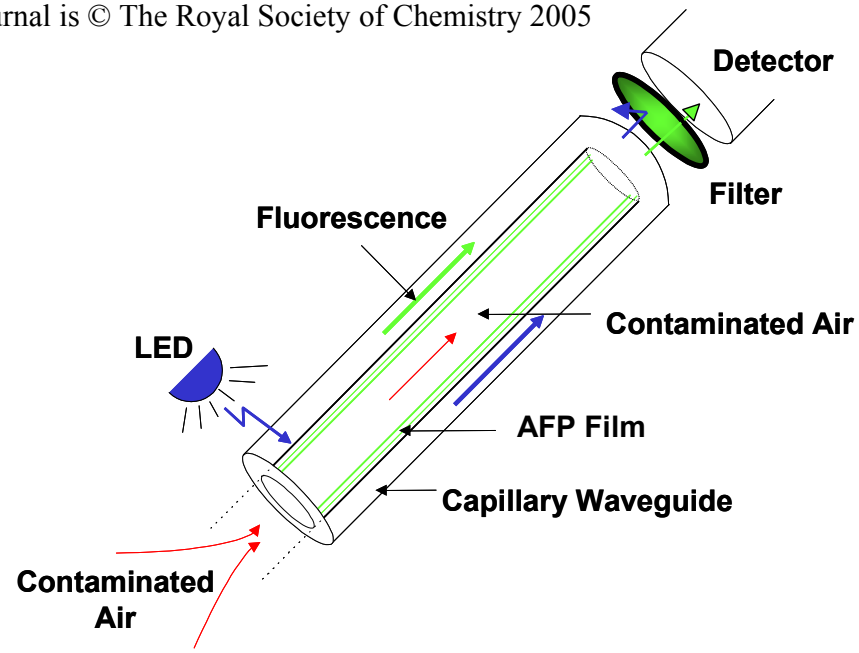
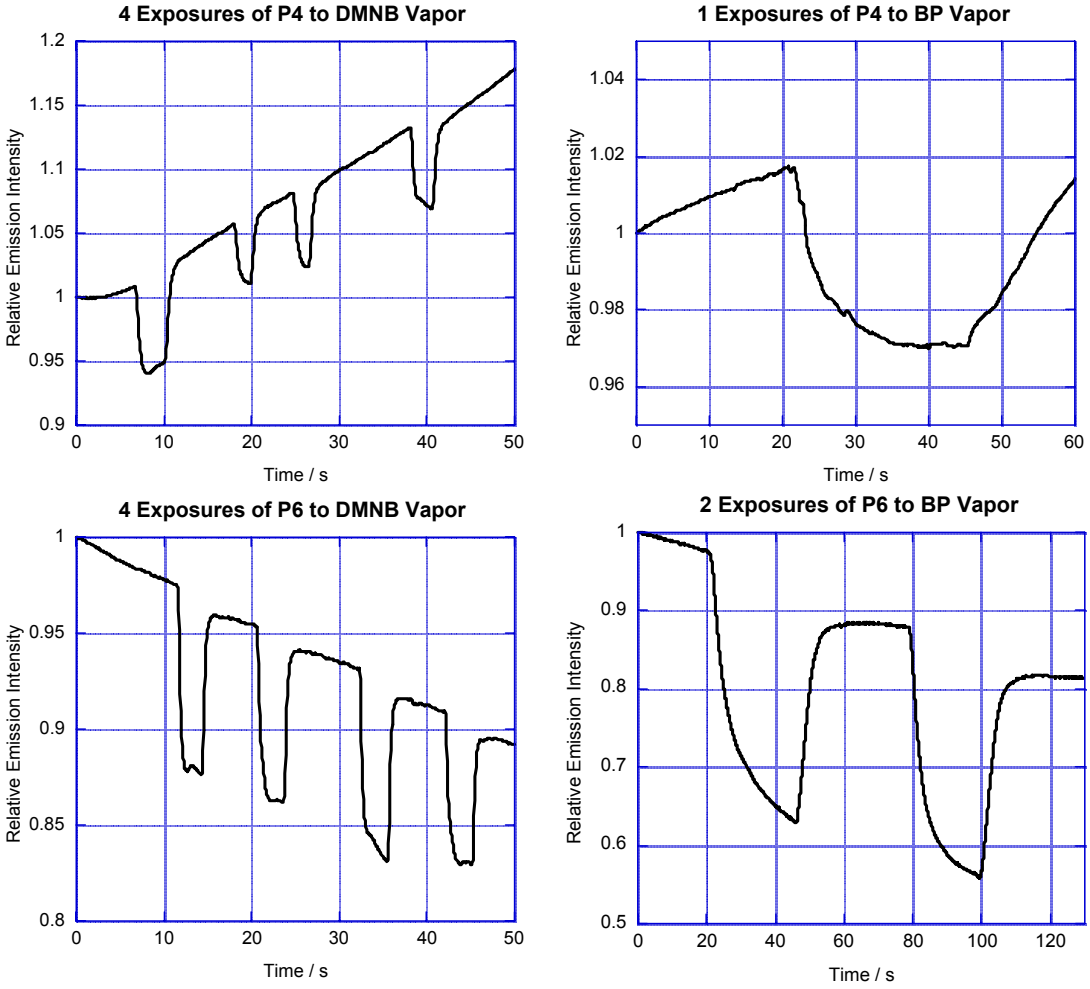


Schematic of how the Nomadics Fido detects fluorescence intensity modulations as a function of analyte vapor.



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