Trace Hydrazine Detection with Fluorescent Conjugated Polymers: A Turn-On Sensory Mechanism**

By *Samuel W. Thomas, III*, and *Timothy M. Swager**

Hydrazine, a heavily used industrial chemical, has been implicated as a carcinogen and is readily absorbed through the skin.[1] Its strong reducing power has led to its use as an oxygen scavenger and corrosion inhibitor in various applications involving water-heating systems, as well as a fuel in rocket-propulsion systems. As a result of its toxicity and reactivity, facile detection of hydrazine is also relevant to homeland security. Traditional analytical methods utilized for hydrazine detection include spectrophotometric detection,[2,3] as well as assorted electrochemical schemes.[4,5] The expansion of conjugated polymer sensory materials[6] has also led to their application towards the detection of hydrazine. Of primary interest have been the conducting properties of polypyrrole,[7] polythiophene,[8] and polyaniline.[9–11]
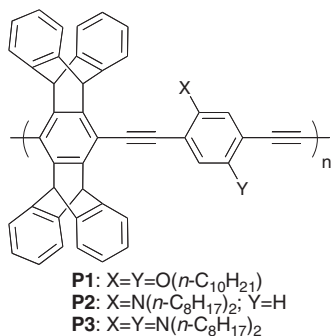
To our knowledge, however, amplifying fluorescent polymers (AFPs) have not been explored for hydrazine detection. AFPs show very high sensitivities to quenching analytes such as 2,4,6-trinitrotoluene (TNT) via a photoinduced electron-transfer quenching ("turn-off") mechanism.[12] This sensitivity of fluorescence quenching is due to a combination of inter- and intrachain exciton transport in thin films. Herein we report a "turn-on" fluorescence detection method for hydrazine vapor with AFPs.

We investigated several polymers (**P1**–**P3**) for hydrazine detection. These conjugated polymers are structurally related

P1: X=Y=O(*n*-C$_{10}$H$_{21}$)
P2: X=N(*n*-C$_8$H$_{17}$)$_2$; Y=H
P3: X=Y=N(*n*-C$_8$H$_{17}$)$_2$

[*] Prof. T. M. Swager, S. W. Thomas, III
Department of Chemistry, Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139 (USA)
E-mail: tswager@mit.edu

poly(phenylene ethynylene)s (PPEs), varying in their degree of electron density along the polymer chain. The response of **P3** to saturated hydrazine vapor (10 s exposure) is given in Figure 1.[13] It is clear from Figure 1 that no new emitting species were generated by exposure to hydrazine since the spectral shape does not change. In addition, the excitation spectrum of the polymer remained the same after the introduction of hydrazine. The other conjugated polymers investigated also showed no change in the shape of their emission spectra upon exposure to hydrazine vapor (see Supporting Information).
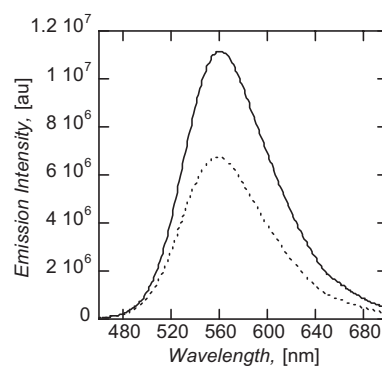
Figure 1. Emission spectra of **P3** before (dotted) and after (solid) exposure to a equilibrium vapor of hydrazine for 10 s.

We have also compared the relative emission enhancements of these polymer films upon exposure to saturated hydrazine vapor. The aryl diamine containing polymer **P3** gave larger average emission enhancements than the less-electron-rich **P1** or **P2** when exposed to saturated hydrazine vapor. Therefore, the most readily oxidized polymer gave the largest emission enhancement.

In addition, this enhancement was not observed in solution upon addition of hydrazine. This lack of a solution-phase enhancement suggests that there are a small number of quenching sites within the thin films of the readily oxidized polymers. Exciton and energy migration in conjugated polymers is much more efficient in the solid state than in solution, and the presence of a small number of quenching sites within a thin film can cause a large degree of fluorescence quenching. This is the reason why sensing highly electron-deficient analytes like TNT is so efficient with these materials.[12]

These three observations, combined with the reducing nature of hydrazine, have led us to propose that the transduction mechanism for emission enhancement with these materials is

an "unquenching" type of mechanism, in which the addition of hydrazine vapor eliminates a non-radiative decay pathway of the conjugated polymer, resulting in a higher solid-state quantum yield of the conjugated polymer. The non-radiative decay pathway that is suppressed upon addition of hydrazine is likely quenching by a small number of oxidized trap sites along the polymer backbone. The removal of these traps by reduction with hydrazine vapor leads to a large fluorescence increase, which is larger for materials that are more prone to oxidation under ambient conditions. This proposed mechanism is essentially the reverse of the process by which AFPs detect electron-poor analytes by fluorescence quenching.[12]

We have applied this scheme to the detection of trace hydrazine vapor. Figure 2 illustrates the response of a partially photobleached film of **P2** to 1 ppm (permissible exposure limit) of hydrazine vapor. In order to acquire reproducible quantitative data, the polymer films were coated on the inside of a glass capillary and analyzed in a Fido sensory platform.[14]
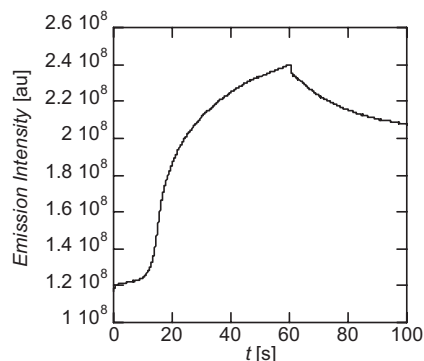
Figure 2. Time-dependent emission of a photobleached film of **P2** in a Fido sensing platform exposed to 1 ppm hydrazine vapor for 60 s.

This device allows for the collection of fluorescence intensity data of a thin film while it is exposed to a continuous flow of analyte vapor. Low concentrations of hydrazine analyte were generated by flowing nitrogen gas past a heated permeation tube with a known rate of hydrazine diffusion. Adjusting the flow rate of N_2 allowed for the preparation of a dilute gas-phase sample of hydrazine with a known concentration. Photo-oxidation by simple irradiation in ambient atmosphere at the excitation wavelength for 2–3 min increased the number of oxidized traps along the polymer backbone, as was evidenced by the decrease in fluorescence intensity as a function of irradiation time. This photobleaching procedure allowed for a larger on/off ratio upon exposure to hydrazine vapor. This observation also supports our proposed transduction mechanism (see above). We have observed turn-on signals at concentrations as low as 100 ppb (10 % of the permissible exposure limit) hydrazine vapor (See Supporting Information). These low detection thresholds highlight the amplified nature of the signal-transduction mechanism.

The intentional inclusion of traps by I_2 doping gave a system with a much lower background signal while maintaining the amplified nature of the transduction. Figure 3 illustrates the UV/vis spectra of a thin film of polymer **P3** upon exposure to iodine and hydrazine. Exposure to iodine resulted in a significant spectral change of **P3**, whereas the polymers that are
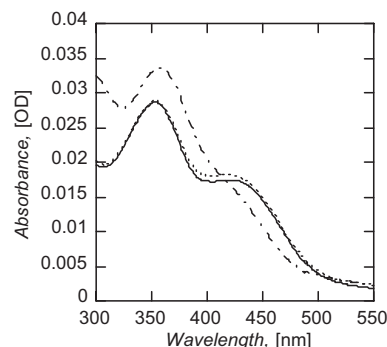

Figure 3. UV/vis spectra of a film of **P3** before (solid) and after (dot–dash) exposure to I_2 vapor. The dotted line is the spectrum after exposure of the doped film to saturated hydrazine vapor for 5 s.

more difficult to oxidize (**P1** and **P2**) showed no evidence of chemical reaction with I_2 (Supporting Information). All three polymers showed almost complete fluorescence quenching upon exposure to saturated I_2 vapor. The observed fluorescence quenching of **P1** and **P2** by I_2 vapor is likely due to intercalation of I_2 rather than chemical oxidation. Exposure of the oxidized **P2** to saturated hydrazine vapor resulted in a nearly full recovery of solid-state emission with identical spectral shape (Fig. 4) by reduction of oxidized polymer chains and intercalated iodine. Figure 5 illustrates the reproducibility of the process over multiple iodine/hydrazine exposure cycles for the more readily oxidized **P3**.

We have also applied the use of molecular iodine as a sacrificial oxidant vapor to trace hydrazine detection. Figure 4 illustrates the time-dependent fluorescence response of a thin film of iodine-doped (exposed to saturated iodine vapor for ~1 s) **P2** to 1 ppm hydrazine vapor in a Fido sensing platform. The on/off ratio of this sensory material was much larger than with the pure polymer, since the intercalated iodine almost completely quenched the emission of the film. In this example, there was a fluorescence enhancement of almost one order of magnitude within 5 min.

Our approach to hydrazine detection has several advantages. The high sensitivity of fluorescence spectroscopy allows for the reliable detection of very small changes in fluorescence intensity. Also, this type of "turn-on" fluorescence sensory scheme is preferable to the more common "turn-off" mechanism, since there are far fewer potential interferents that could cause a false positive with an emission increase. The primary interferents of this detection scheme are other amines such as ammonia. These are typical interferents in hy-
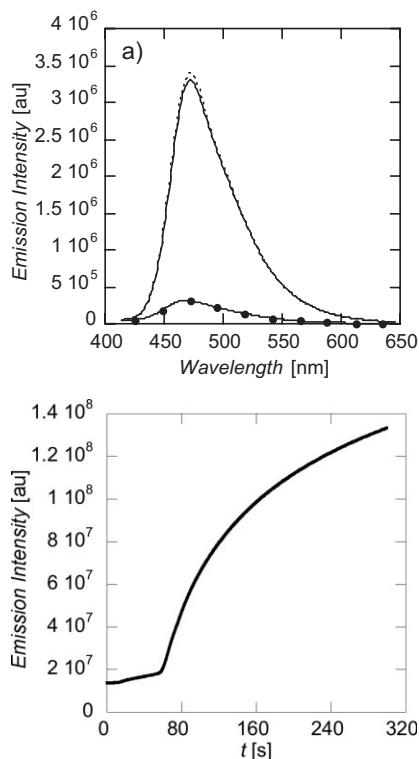
Figure 4. a) Emission response of **P2** before (dotted line) and after (solid line with circles) exposure to equilibrium iodine vapor for approximately 5 s, followed by exposure to equilibrium hydrazine vapor (solid line). b) Fluorescence trace of I_2 doped **P2** exposed to 1 ppm hydrazine.
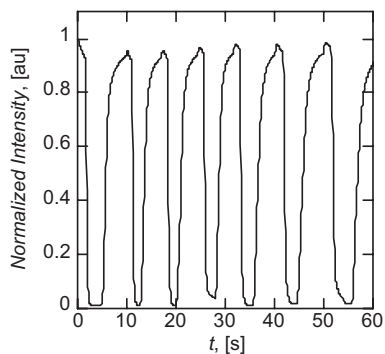
Figure 5. Plot showing normalized emission intensity of a film of **P3** upon exposure to saturated iodine vapor (quench) followed by saturated hydrazine vapor (recovery). This plot demonstrates the reversibility of hydrazine sensing by this method.

drazine detection schemes that rely upon reduction as the transduction chemistry.[7,8] However, as has been noted with these other hydrazine-detection schemes, these simple amines are not strong interferents at low concentrations, with a 50 ppm concentration of ammonia giving a signal increase (20 %) at least an order-of-magnitude less than that observed with 1 ppm hydrazine. Organic solvents such as tetrahydrofuran or methanol showed no interfering behavior.

In summary, we have presented an amplified turn-on sensory scheme for hydrazine vapor using fluorescent conjugated polymers. More readily oxidized polymers such as **P3** gave larger on/off ratios upon exposure to hydrazine and are more likely to be useful in this application. Our proposed mechanism involves a small number of oxidized sites within conjugated polymer films being reduced by hydrazine vapor to give large increases in fluorescence intensity. This type of "unquenching" mechanism is essentially the reverse of amplified detection by fluorescence quenching of conjugated polymer films in response to electron-poor analytes. The intentional introduction of iodine as a reducible quencher and oxidant reduced the intensity of the background fluorescence signal in trace-detection experiments. In addition, we anticipate that hydrazine exposure of functional conjugated-polymer films (e.g., for explosives detection) that have lost a portion of their solid-state emission due to aging or photobleaching may allow for the extension of their useful lifetimes. Future work will focus on the optimization and expansion of this scheme towards other toxic reducing agents.

Experimental

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 (for solution measurements) or a blank cover slip (for solid-state measurements). Emission spectra were acquired on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using front-face detection for all film samples.

Materials: Hydrazine hydrate and iodine were purchased from Aldrich and used as received. The preparation and characterization of all polymers investigated in this study has been previously described [12,13].

Solid-State Spectroscopy: Thin films for spectroscopy were spin-cast onto glass cover slips from an approximately 1 mg mL^{-1} chloroform solution at 1500–3000 rpm. Experiments involving equilibrium vapor pressure hydrazine were performed by using a 20 mL vial that included a piece of cotton and approximately 3 drops of hydrazine hydrate. For spectral responses, this vial was held up to the surface of the film for several seconds. A similarly simple procedure was followed for iodine doping.

Time-Dependent Solid-State Measurements: The temporal responses of the emission signals of **P1**–**P3** to hydrazine vapor were measured using a Fido sensing platform manufactured by Nomadics, Inc. (http://www.nomadics.com). The inside of a glass capillary was coated with the conjugated polymer film (spun-cast from a 1 mg mL^{-1} solution (tetrahydrofuran or CHCl$_3$ at 700 rpm for 1 min). This capillary was inserted into the sensor, which was equipped with a laser diode (405 nm) and a photodetector. In addition, a pump, operating at 30–60 cc min^{-1} drew in air from a nozzle through the capillary, exposing the film to an analyte vapor of the user's choice (in this work, hydrazine or iodine). The total emission was then continuously monitored. Equilibrium concentrations of vapors were introduced by manually holding a vial (20 mL) containing a small amount of the analyte and a piece of cotton up to the nozzle of the Fido device. Trace concentrations of hydrazine or ammonia were introduced into the Fido device by flowing a known rate of dry nitrogen gas (using a flow meter) through a chamber with controllable temperature. This chamber contained a disposable hydrazine permeation tube (Kin-Tek Laboratories) with a known rate of diffusion. By adjusting the rate of gas flow over the permeation tube, the trace concentration of hydra-

zine in the gas flow could be accurately changed. Films used for trace hydrazine detection were first irradiated with the Fido light source until they achieved a stable baseline, which typically resulted in an overall weakening of the fluorescence signal. Iodine doping in Fido experiments was achieved by presenting a vial of iodine crystals to the instrument.

[1] *The Merck Index*, 12th ed. (Ed: S. Budavari), Merck Research Laboratories, Whitehouse Station, NJ **1996**, p. 816.

[2] a) J. Mañes, P. Campillos, G. Font, H. Martre, P. Prognon, *Analyst* **1987**, *112*, 1183. b) P. Ortege-Barrales, A. Molina-Díaz, M. I. Pascual-Reguera, L. F. Capitán-Vallvey, *Anal. Chim. Acta* **1997**, *353*, 115.

[3] A. M. Haji Shabani, S. Dadfarnia, K. Dehghan, *Bull. Korean Chem. Soc.* **2004**, *25*, 213.

[4] a) J. Wang, Z. Taha, *Talanta* **1988**, *35*, 965. b) J. M. Pingarrón, I. Ortiz Hernández, A. González-Cortés, P. Yañez-Sedeño, *Anal. Chim. Acta* **2001**, *439*, 281.

[5] J. Wang, L. Chen, *Anal. Chem.* **1995**, *67*, 3824.

[6] a) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537. b) T. M. Swager, *Acc. Chem. Res.* **1998**, *31*, 201.

[7] N. Ratcliffe, *Anal. Chim. Acta* **1990**, *239*, 257.

[8] D. L. Ellis, M. R. Zakin, L. S. Bernstein, M. F. Rubner, *Anal. Chem.* **1996**, *68*, 817.

[9] J. Huang, S. Virji, B. H. Weiller, R. B. Kaner, *Chem. Eur. J.* **2004**, *10*, 1315.

[10] S. Virji, J. Huang, R. B. Kaner, B. H. Weiller, *Nano Lett.* **2004**, *4*, 491.

[11] S. Virji, R. B. Kaner, B. H. Weiller, *Chem. Mater.* **2005**, *17*, 1256.

[12] J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11 864.

[13] S. W. Thomas, III, T. M. Swager, *Macromolecules* **2005**, *38*, 2716.

[14] The Fido sensor is commercially available from Nomadics Inc. and was originally developed for explosives detection. C. Cumming, C. Aker, M. Fisher, M. Fox, M. laGrone, D. Reust, M. Rockley, T. M. Swager, E. Towers, V. Williams, *IEEE Trans. Geosci. Remote Sensing* **2001**, *39*, 1119.