

AgBF₄-Impregnated Poly(vinyl phenyl ketone): An Ethylene Sensing Film

Omar Green, Nickolaus A. Smith, Arthur B. Ellis, and Judith N. Burstyn*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received October 23, 2003; E-mail: burstyn@chem.wisc.edu

Sensors that can detect a wide variety of analytes are of current interest.¹ Herein we report the basis for an optical sensor for ethylene, employing a polymer film that luminesces in the presence of bound silver ions. Upon exposure to ethylene, the metal ion mediates quenching of the polymer's photoluminescence (PL). This sensing method is potentially applicable to many metal ions and analytes.

We have developed this ethylene-responsive film for two reasons: ethylene is a plant hormone responsible for the loss of millions of dollars of fresh produce,² and ethylene's limited chemical functionality makes it a particular challenge to detect. Currently, metal oxide resistivity^{3a} and ozone-mediated chemiluminescence^{3b} sensors are used to detect ethylene commercially; however, devices employing these methods are expensive and do not meet the sensitivity requirements for shipping and storing produce. The film, which is based on facilitated transport technology,⁴ is comprised of silver tetrafluoroborate (AgBF₄)-impregnated poly(vinyl phenyl ketone) (PVPK) and produces a reversible PL quench in response to ethylene. The simplicity of preparation, the inexpensive nature of the reagents, and the sensitivity afforded by luminescence make this method a potential improvement on present ethylene-sensing technology.

Photoluminescent films of AgBF₄-impregnated PVPK respond to ethylene with changes in emission intensity (Figure 1, s1 ("s" indicates Supporting Information)). Films were prepared on glass slides by deposition from CH₃CN or THF solutions of PVPK and AgBF₄.⁵ Only films containing a 2:1 molar ratio of Ag⁺ to PVPK acetophenone groups responded to ethylene with a consistent and reversible PL quench.⁶ There were no changes in PL when a nonimpregnated PVPK film was exposed to ethylene or when an impregnated film was exposed to Ar or air. Changes in emission intensity in response to ethylene were observed only when films contained the Ag⁺ ion; films containing NaBF₄ in a 2:1 ratio of Na⁺ to PVPK functional groups showed no response to ethylene. To obtain a PL quench that was reversible and proportional to ethylene pressure, a conditioning process was required.⁷ Studies of CH₃CN-cast films indicated that there was a loss of Ag⁺-bound CH₃CN upon conditioning (vide infra). Parallel studies of films cast from THF revealed that a single conditioning cycle produced reproducible PL quenching; however, THF-cast films were more sensitive to photodegradation than CH₃CN-cast films. After conditioning, films responded to ethylene, propylene, or ammonia with a reversible quench.

Conditioned films exhibited responses that were proportional to pressures of ethylene between 20 and 150 Torr,⁸ above which concentration the response saturated (Figure 1, s1). The films responded similarly when exposed to ethylene alone or to ethylene diluted with Ar or laboratory air (50% humidity, 27 °C). Stern–Volmer analysis⁸ of the PL response of CH₃CN-cast films implicates sites that are accessible and sites that are inaccessible to ethylene, as demonstrated by the plot's deviation toward the abscissa (Figure 2). The modified Stern–Volmer plot (Figure 2,

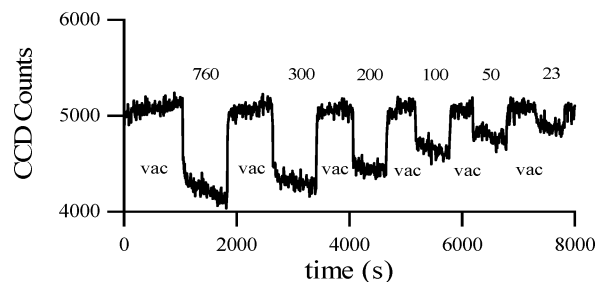


Figure 1. Representative plot of changes in PL intensity vs time resulting from exposure to the indicated pressures of ethylene (Torr) for a 2:1 AgBF₄-PVPK film cast from CH₃CN.

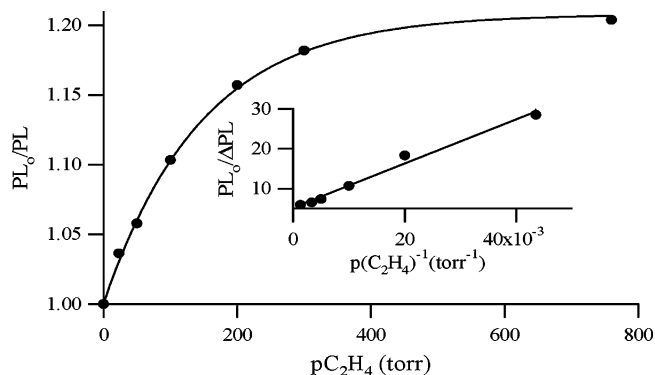


Figure 2. Stern–Volmer analysis of PL data from Figure 1 with line of best fit ($\chi^2 = 7.71 \times 10^{-5}$). In a modified Stern–Volmer plot of the data (inset), the y-intercept reveals that $19.5 \pm 2.5\%$ of possible luminescent active sites are quenched by ethylene, and the slope reveals a binding constant of $K_{SV} = 9.37 \pm 1.25 \times 10^{-3} \text{ Torr}^{-1}$ for these accessible sites.

inset), where the intercept gives the percentage of PL quenched at infinite quencher concentration, suggests that $19.5 \pm 2.5\%$ of the emissive sites are accessible to ethylene. Diffusive access of ethylene to the emissive sites may not be the only limitation on the response. Heterogeneity within the film may result in a fraction of emissive sites that are unresponsive to ethylene due to local coordination structure.

The molecular changes that occur during film deposition, conditioning, and sensing were investigated using IR spectroscopy.⁹ Three regions of the IR spectrum provide signature vibrations: (1) 1400–1800 cm⁻¹, containing the carbonyl stretches (1620–1700 cm⁻¹) and the aromatic C=C stretches (1430–1620 cm⁻¹), (2) 2200–2400 cm⁻¹, containing the nitrile stretches, and (3) 2800–3200 cm⁻¹, containing the aromatic C–H stretch from the phenyl moiety (3064 cm⁻¹) and the aliphatic C–H stretches from the polymer backbone (ca. 2950 cm⁻¹) and from acetonitrile (2947 cm⁻¹) (Figure 3).^{10,11} The ν_3 mode of the BF₄⁻ counterion, centered at 1050 cm⁻¹, reports on the anion's environment within the polymer matrix (Figure s2).

Incorporation of AgBF₄ into PVPK induces changes in both the metal salt and the polymer vibrations, suggestive of modest metal ion/polymer interaction. Deposition of a 2:1 film from a solution

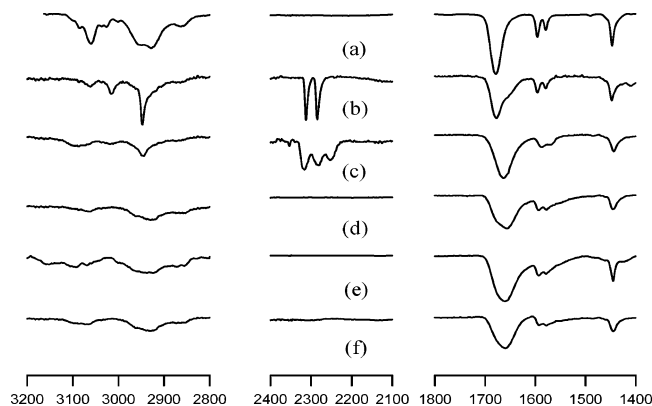


Figure 3. IR spectra of a CH_3CN -cast film during conditioning and sensing: C–H region (left), nitrile region (center), and C=O/C=C region (right). (a) PVPK, (b) 2:1 AgBF_4 -PVPK film as cast, (c) 2:1 film after one conditioning cycle,⁷ (d) 2:1 film after six conditioning cycles, (e) 2:1 film after exposure to 1 atm ethylene (under Ar), (f) 2:1 film after exposure to 1 atm ethylene (under vacuum).

of AgBF_4 and PVPK in CH_3CN results in stable incorporation of CH_3CN into the film. This CH_3CN is coordinated to the Ag^+ ions, as evidenced by the characteristic $\nu_{\text{C-H}}$ (2947 cm^{-1}) and $\nu_{\text{C}\equiv\text{N}}$ (2313 and 2285 cm^{-1}) modes (Figure 3b),¹¹ and is resistant to removal under dynamic vacuum. Within the film, the environment of the BF_4^- counterion is distinct from that encountered in pure AgBF_4 , as evidenced by multiple minima in the ν_3 mode (Figure s2). The polymer carbonyl groups are affected by incorporation of AgBF_4 , and a subset (54–59%, Table s1) of these carbonyl groups shows a decrease in $\nu_{\text{C=O}}$, from 1680 to 1656 cm^{-1} (Figure 3b, s3), indicative of coordination to the Ag^+ ion. A broadening of the C=C stretches of the polymer phenyl groups at 1444 cm^{-1} is also observed.

The conditioning process involves the gradual loss of Ag^+ -coordinated CH_3CN concurrent with increased Ag^+ coordination to the carbonyl groups and phenyl rings of PVPK. After one conditioning cycle, significant changes in the CH_3CN stretches are observed (Figure 3c). The $\nu_{\text{C}\equiv\text{N}}$ modes of the coordinated CH_3CN broaden, and a new peak, consistent with free CH_3CN trapped within the polymer matrix, appears at 2252 cm^{-1} . The C–H stretch of the CH_3CN methyl group also broadens. Concurrently, polymer modes shift and broaden, indicative of increasing interaction between the polymer functional groups and the Ag^+ ions. After six conditioning cycles, no CH_3CN remains within the film, as evidenced by the absence of nitrile features (Figure 3d). The polymer carbonyl resonance exhibits a minimum 22 cm^{-1} lower in frequency than that observed for free PVPK, consistent with coordination of 89–91% (Table s1) of the carbonyl groups to Ag^+ (Figure s3). The phenyl C=C and C–H modes are broadened, suggesting that the phenyl rings also interact with the Ag^+ ions. After conditioning, the ν_3 mode of the BF_4^- counterion shows two distinct minima, consistent with a low-symmetry environment for the counterion (Figure s2).

Minor changes observed upon binding ethylene suggest that the polymer carbonyls remain coordinated to Ag^+ while the phenyl rings may be displaced. Ethylene does not displace the polymer carbonyl groups from the coordination sphere of the Ag^+ ions, as there is minimal change in the polymer carbonyl resonance upon exposure to ethylene (Figure 3d,e,f). Approximately the same percentage of carbonyl groups is bound to Ag^+ ions before, during, and after binding ethylene (Figure s3, Table s1). In contrast, the phenyl C=C mode at 1444 cm^{-1} exhibits a reversible change in peak width upon exposure to ethylene (Figure s4, Table s2.) The similarity in peak width between free PVPK and ethylene-bound

Ag^+ -impregnated PVPK suggests that the phenyl rings may be displaced from the Ag^+ coordination sphere by ethylene. Minimal changes in the other polymer modes and in the $\text{BF}_4^- \nu_3$ mode (Figure 3d,e,f and s2) suggest that the gross morphology of the film is not significantly perturbed upon interaction with ethylene.

In summary, an AgBF_4 -impregnated PVPK film with a 2:1 ratio of Ag^+ ions to polymer functional groups demonstrated a reversible and proportional response to ethylene pressures ranging over 1 order of magnitude. The Stern–Volmer model suggested that the response is due to interaction of ethylene with ca. 20% of the luminescent sites in the film. Infrared spectroscopy revealed that Ag^+ ions coordinate to the polymer carbonyl and phenyl groups in the active sensing film. We hypothesize that luminescence quenching by ethylene is mediated by simultaneous coordination of Ag^+ to the polymer carbonyl groups and to ethylene by either of two mechanisms: displacement of the phenyl rings from the Ag^+ ions or enhancement of vibrational relaxation. These studies illustrate a sensing paradigm in which metal coordination enables sensing of a simple gas with luminescent organic polymers.

Acknowledgment. This work was supported by the National Institutes of Health (HL65217-04, J.N.B.), and is based in part upon work by A.B.E., while serving at and supported by the National Science Foundation.

Supporting Information Available: Absorption/emission spectra, and analysis of IR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Mitrovics, J.; Ulmer, H.; Weimer, U.; Gopel, W. *Acc. Chem. Res.* **1998**, *31*, 307–315.
- Willis, R. B. H.; Warton, M. A.; Ku, V. V. *Aust. J. Exp. Agric.* **2000**, *40*, 465–470.
- (a) Dong, Y.; Li, W.; Yu, C.; Jiang, Y. *Cn. Pat.* 1228535, 1999. (b) Nelson, B. N.; Richard, R. V., II; Kane, J. A. *Intl. Pat. Appl.* 023791, 2000.
- (a) Safarik, D. J.; Eldridge, R. B. *Ind. Eng. Chem. Res.* **1998**, *37*, 2571–2581. (b) Kim, Y. H.; Ryu, J. H.; Bae, J. Y.; Kang, Y. S.; Kim, H. S. *Chem. Commun.* **2000**, 1261–1262. (c) Yoon, Y.; Won, J.; Kang, Y. S. *Macromolecules* **2000**, *33*, 3185–3186. (d) Jin, J. H.; Hong, S. U.; Won, J.; Kang, Y. S. *Macromolecules* **2000**, *33*, 4932–4935.
- Films with varying concentrations of AgBF_4 were prepared by a common procedure; preparation of a 2:1 AgBF_4 -PVPK functional group (carbonyl or phenyl) film is as follows. PVPK ($M_n = 2847$) and AgBF_4 were purchased from Aldrich and used as received. PVPK (35 mg) and AgBF_4 (100 mg) were dissolved in distilled CH_3CN (CaH_2) or THF (Na/benzophenone) to a total volume of 6 mL. The AgBF_4 /PVPK solution (0.2 mL) was deposited on a microscope slide, and the solvent was allowed to evaporate in air. Once the film had adhered, the slide was placed in a PL cell and the film was dried under vacuum for 2–4 h.
- The glass slide bearing the film was mounted inside a Schlenk luminescence cell. The film was excited with 0.5–3.0 mW of 488-nm light from a Coherent Innova 90-4C Ar ion laser. Emission was monitored with an Oriol Multispec 77400 CCD detector via fiber optic probe. For each experiment the emission profile was recorded, and the PL intensity at the emission maximum (575 nm) was monitored in response to changes in the ambient atmosphere of the film. Conditions tested were 1 atm Ar and air, vacuum, and pressures of ethylene ranging from 0 to 760 Torr. There was no change in the maximum emission wavelength in any experiment.
- To condition the film, the atmosphere was cycled between 1 atm ethylene and vacuum (6 cycles over 6 h for CH_3CN -cast films, 1 cycle over 1 h for THF-cast films), until the emission under vacuum was constant.
- Conditioned films were exposed to varying pressures of ethylene, and the PL response was measured. Reversible and proportional responses were also observed for propylene. Stern–Volmer analysis was performed according to Lakowicz (Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999). Data were analyzed with the IGOR Pro graphical analysis program.
- Films of 2:1 AgBF_4 -PVPK functional groups were prepared on NaCl plates in a drybox. The film-bearing plate was mounted in an IR cell designed for facile exchange of the ambient gas atmosphere. IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer; the spectra reported are averages of 32 scans. The film was conditioned by cycling between vacuum and 700 Torr ethylene. All spectra were recorded under vacuum except the spectrum of the ethylene-exposed film, which was recorded after ethylene had been flushed from the cell with a constant flow of argon for ca. 10 min.
- Gambi, A.; Giorgianni, S.; Passerini, A.; Visinoni, R.; Gherseti, S. *Spectrochim. Acta, Part A* **1980**, *36A*, 871–878.
- Manz, G. J.; Tait, M. J.; Meier, J. *J. Phys. Chem.* **1967**, *71*, 963–968.

JA039203O