

Optical sensing of amine vapors with a series of tin compounds†

Evonne A. Baldauff^a and Jillian M. Buriak^{*a,b}^a Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084, USA^b Department of Chemistry, the National Institute for Nanotechnology (NINT), University of Alberta, Edmonton, AB, T6R 2Z4, Canada. E-mail: jhuriak@ualberta.ca

Received (in West Lafayette, IN, USA) 27th April 2004, Accepted 23rd June 2004

First published as an Advance Article on the web 30th July 2004

Certain common Sn²⁺ salts exhibit bright luminescence of various optical wavelengths upon excitation with 254 nm UV irradiation at room temperature. Light emission can be selectively quenched by exposure to low concentrations of amines, and can in some cases be regenerated with either a nitrogen purge or exposure to acid vapors, rendering the compounds useful for application in optical sensing arrays.

Sensor arrays, typically comprised of metal oxides, are an area of intense interest because of their utility for electronic nose applications and provide a highly selective means of vapor detection. The sum of the individual component responses generates a unique signature of the exposed vapor. In addition to electronic response patterns, similar arrays have been designed to utilize a visual response as a means for identification. Sailor and co-workers¹ incorporated reflectivity and photoluminescence changes of porous silicon to enhance array sensitivity while Suslick and Rakow² exploited the individual color change patterns in a series of metalloporphyrins to repetitively detect and identify certain coordinating gases. The sensing of amines, in particular, is important in a number of industrial contexts, including the food industry.³

Here we report a small optical sensing array comprised solely of luminescent tin(II) compounds that are selectively quenched by amine vapors in either air and nitrogen. These quenching events are consistently reproducible and can be detected at concentrations as low as 100 ppb. Reversibility varies for each different tin compound, but simple nitrogen flush or exposure to acid vapor can bring about full or partial restoration of the initial emission intensity.

The role of divalent tin as an s² type luminescent center within a host lattice has been thoroughly examined,⁴ and several photoluminescent Sn²⁺ and Sn⁴⁺ compounds have also been reported over a wide temperature range.^{5–9} Tin(IV) oxide, a prevalent semiconducting sensor material, has been shown to luminesce at elevated temperatures in monocrystalline¹⁰ and more recently, nanocrystalline¹¹ form. In order to prepare a convenient optical sensing array, we chose to examine only those salts with emission at ambient temperatures.

Of the compounds for which photoluminescence spectra are reported, only tin(II) sulfate, which emits *via* self-trapped exciton emission, fits this description.⁶ We have, however, determined that other tin(II) salts, such as tin(II) methanesulfonate, tin(II) triflate, and tin(II) fluorophosphate, also display visible emission at room temperature after examining a wide range of compounds (supplementary materials). The effect of amine vapors upon the light emission of these four tin salts provides the basis for the optical sensing components of the array.

The tin salts were used as-purchased except for tin(II) methanesulfonate which was first isolated from aqueous solution. If desired, the powders can be pressed into pellet form with no alteration of emission or quenching effects as compared to the powdered samples. Similarly, no differences were observed between purchased salts and those prepared *via* literature procedures.¹² Gas concentrations were prepared with standard mass flow control

units (Cole-Parmer) and introduced into a quartz cell containing the tin salts. Both static and continuous vapor flow methods yielded analogous results. The samples were excited at 254 nm with an Hg/Xe lamp and emission was measured directly with a liquid nitrogen-cooled CCD spectrophotometer. When the array was exposed to an amine vapor a distinct, reproducible decrease in the light emission could be observed in particular array members, as shown visually in Fig. 1.

The photoluminescence quenching enables selective detection of amine vapors from other analytes (Fig. 2), and from mixtures. Acetone did show a slight quenching effect with Sn(CH₃SO₃)₂, but was small relative to diethylamine quenching at the same concentration. Similar quenching events were not observed with other nucleophilic functionalities, including a basic phosphine (tri-*n*-butyl phosphine), as shown in the supplementary materials. More important was the observation that each tin(II) salt responds differently to the five amines shown in Fig. 3, and thus similar analytes can be distinguished at a normalized concentration (Table 1). For example, when the salts were exposed to ammonia, only the emission from Sn(CF₃SO₃)₂ was affected, but upon exposure to pyridine each member yielded a diminished optical signal, allowing differentiation between low concentrations of the two

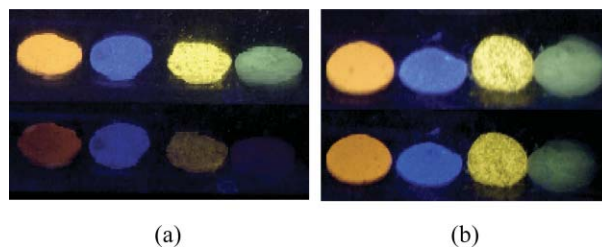


Fig. 1 Visible detail of the initial *versus* diminished light emission seen from the array of Sn²⁺ pressed pellets (left to right: SnSO₄, SnPO₃F, Sn(CH₃SO₃)₂, Sn(CF₃SO₃)₂) when exposed to (a) 100 ppm of pyridine and (b) 1 ppm pyridine.

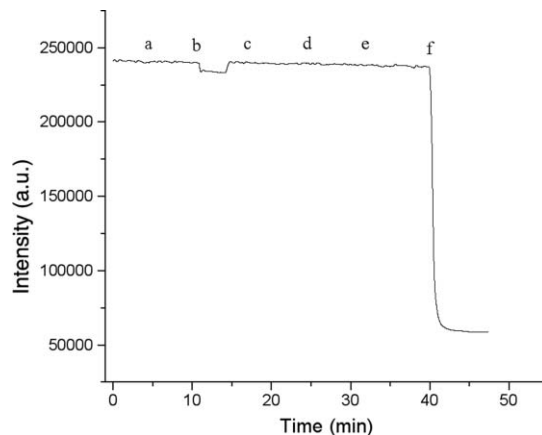


Fig. 2 Tin(II) methanesulfonate exposed to 50 ppm of (a) dichloromethane, (b) acetone, (c) diethyl ether, (d) pentane, (e) ethanol, (f) diethylamine. (a)–(e) were exposed to the analyte for ~5 minutes and then briefly purged with nitrogen before the next analyte was introduced.

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b4/b406230b/>

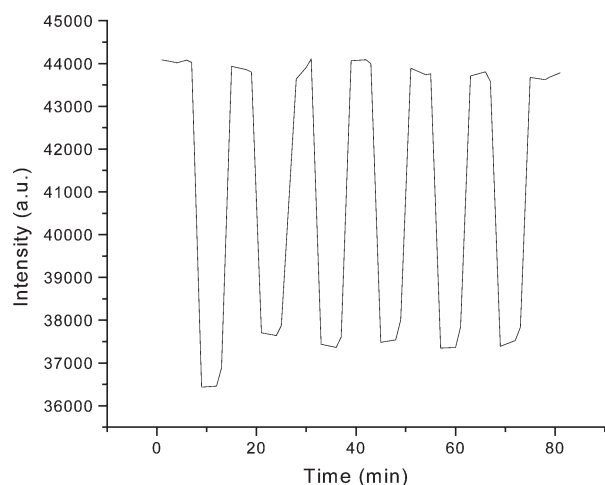
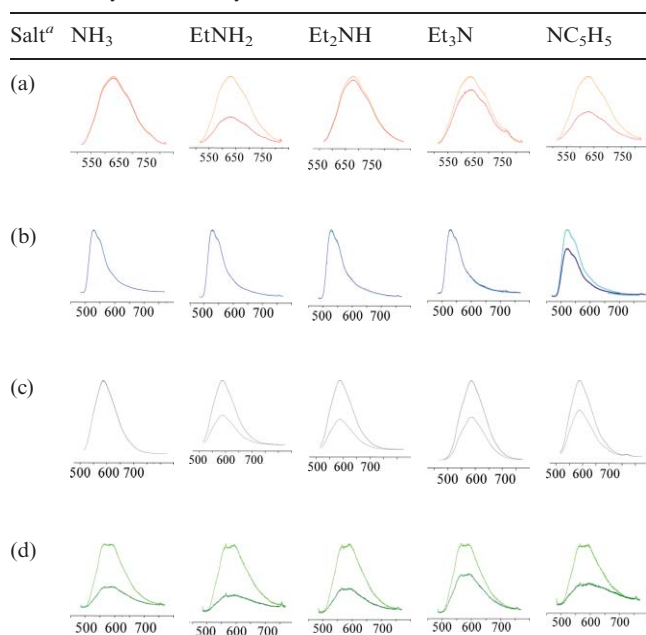


Fig. 3 Reversibility cycling of SnPO₃F with a concentration of 10 ppm pyridine followed by an N₂ purge. After exposure to pyridine, the system was held for 5 minutes and then flushed with nitrogen for 5 minutes before the next pyridine exposure.

Table 1 Initial photoluminescence and quenching of each salt after exposure to 1 ppm of analyte in nitrogen for 30 seconds. The x axis of each plot is in nm, and the color of the plots reflects the color as observed by the naked eye



^a (a) SnSO₄; (b) SnPO₃F; (c) Sn(CH₃SO₃)₂; (d) Sn(CF₃SO₃)₂.

analytes. SnSO₄ is less sensitive to bulky amines (diethyl- and triethylamine), whereas SnPO₃F only responds to pyridine. Sn(CF₃SO₃)₂ shows no apparent discrimination between amines. Detection limits varied with the individual tin compounds and analytes, but generally the highest sensitivity was observed with pyridine, with a 100 ppb detection limit in all cases with this set-up.

For real world applications, the effect of humidity on the tin(II) sensing material is critical. The light emission from SnSO₄ and SnFPO₃ is unaffected by even 100% humidity in air, while the intensity of Sn(CH₃SO₃)₂ and Sn(CF₃SO₃)₂ drops significantly (supplementary materials). The light emission of the latter two

compounds can be completely regenerated by heating in air to 100 °C for 5 or 20 minutes, respectively, and cycled repeatedly in this way.

The quenching of the light emission by amines was also found to be reversible in some cases. As shown in Fig. 3, the blue emission from SnPO₃F was able to be regenerated with a simple N₂ purge. The results reveal a very quick response time and a complete restoration of light intensity after repeated cycling at a 10 ppm concentration (Fig. 3). This same behavior is observed at 1 ppm and 100 ppm concentrations as well (supplementary materials). Tin(II) methanesulfonate and tin(II) sulfate could be partially regenerated after exposure to trifluoroacetic acid (TFA) vapors. A 14% TFA/air mixture was passed over the salts and light emission was again restored. The intensity levels, however, never reached the initial values and continued to decrease as the cycling continued. No significant regeneration was observed from Sn(CF₃SO₃)₂ when exposed to either an N₂ purge or acid vapors.

The specific method of quenching and reversibility has not yet been determined, but divalent tin has been shown to form complexes with various amine containing molecules¹³ despite the fact that it is less Lewis acidic than tin(IV). We are currently investigating the conditions under which surface binding or absorption of the amine compounds to the surface may occur and thereby provide a pathway for non-radiative decay.

To conclude, the tin(II) salt array provides a quick and convenient way of optically differentiating between similar amine species. The fact that sulfonate groups, R-SO₃⁻ yield light emitting tin(II) compounds at room temperature opens the door to further selectivity *via* tailoring of the R groups. This approach should assist in better understanding the mechanism and furthering the utility of this approach.

We gratefully acknowledge support from the National Science Foundation (USA), the National Research Council (Canada), and the University of Alberta. Dr Hartmut Hedderich is sincerely thanked for technical assistance and John Underwood for assistance with the photographs. J.M.B. is a Camille and Henry Dreyfus Foundation Teacher-Scholar (2002–2004) and a Cottrell Teacher-Scholar of Research Corporation (2000–2005).

Notes and references

- S. E. Letant, S. Content, T. T. Tan, F. Zenhausern and M. J. Sailor, *Sens. Actuators, B*, 2000, **69**, 193.
- N. A. Rakow and K. S. Suslick, *Nature*, 2000, **406**, 710.
- J. Hammond, B. Marquis, R. Michaels, B. Oickle, B. Segee, J. Vetelino, A. Bushway, M. E. Camire and K. Davis-Dentici, *Sens. Actuators, B*, 2002, **84**, 113; M. Dondero, F. Cisternas, L. Carvajal and R. Simpson, *Food Chem.*, 2004, **87**, 543.
- G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Vorlag, New York, 1994.
- A. S. Voloshinovskii, S. V. Myagkota, N. S. Pidsyrailo and Z. A. Khapko, *Opt. Spectrosc.*, 1982, **52**, 760.
- H. Donker, W. M. A. Smit and G. Blasse, *Phys. Status Solidi B*, 1988, **148**, 413.
- H. Kunkely and A. Vogler, *Chem. Phys. Lett.*, 1991, **187**, 609.
- T. Kazuba, K. Era and Y. Ishizawa, *Phys. Lett. A*, 1974, **46**, 413.
- A. S. Voloshinovskii, *Ukr. Fiz. Zh.*, 1982, **26**, 2047.
- H. J. P. Fillard, J. Gasiot, M. DeMurcia and T. T. Quynh, *Phys. Status Solidi A*, 1972, **9**, K196.
- F. Gu, S. F. Wang, C. F. Song, M. K. Lu, Y. X. Qi, G. J. Zhou, D. Zu and D. R. Yuan, *Chem. Phys. Lett.*, 2003, **372**, 451.
- M. A. K. Ahmed, H. Fjellvåg and A. Kjekshus, *Acta Chem. Scand.*, 1998, **52**, 305; R. C. Paul, V. P. Capila and S. K. Sharma, *J. Ind. Chem.*, 1974, **12**, 651.
- J. D. Donaldson, D. G. Nicholson and B. J. Senior, *J. Chem. Soc. A*, 1968, **12**, 2928; D. L. Perry and R. A. Geanangel, *J. Inorg. Nucl. Chem.*, 1974, **36**, 205; K. C. Malloy, M. P. Bigwood, R. H. Herber and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 3709.