

Vapochromic Properties of Nafion Film Doped with Cationic Dyes

Ryoka Matsushima,* Naoko Nishimura, and Yoshiumi Kohno

Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu 432-8561

(Received December 12, 2002; CL-021055)

Protonated Nafion thin film doped with cationic dyes such as flavylium and thionine revealed rapid and vapor-specific color changes (vapochromism) upon exposure to volatile organic compounds. The vapochromic performances were substantially retained after 10 repeated cycles of exposures, implying good reversibility.

Vapochromism of crystalline metal complexes has received considerable attention because of its potential use as color sensors toward environmentally hazardous substances such as volatile organic compounds (VOCs).¹⁻⁶ Contrary, however, vapochromism of organic systems (films or matrices) toward VOCs have been scarcely reported despite its merit of easier fabrication and lower cost, whereas humidity-sensitive color changes of organic polymer films have been reported, e.g., those through switching of the aggregation states of dyes (H- and J-aggregates) induced by adsorbed water molecules in layered assemblies of azobenzene derivatives,^{7,8} a polymethine dye in thin films,⁹ and sulfonephthalain-doped polymers.¹⁰ Optical sensing host dye toward amine vapors has also been reported.¹¹ Color changes by reversible dye aggregation have been well studied in organic systems, e.g., in bilayer membranes,¹²⁻¹⁴ in alkane matrix,¹⁵ on helical DNA template,¹⁶ and in hemicyanine-based bichromophores.¹⁷ This paper is concerned with vapochromism of ionic dyes doped in Nafion thin film, which features much more rapid and extensive color changes upon exposure to VOCs, as compared with dye-doped sugar gels.^{18,19}

A 5 wt% solution of Nafion® was commercially available (through Aldrich Chemicals) and a Nafion film was prepared on a silica glass plate by casting a 1% solution and air-dried overnight at room temperature. The dry film was dipped in a dilute solution of the flavylium perchlorate FV ($1.5 \cdot 10^{-4}$ M) or thionine chloride TH ($3.0 \cdot 10^{-4}$ M) for 5 min, and then dipped in a dilute sulfuric acid (0.5 M) for a few seconds. The acidified film was lightly rinsed by dipping in pure water for a few seconds and air-dried at room temperature, thus giving a protonated Nafion thin film doped with FV or TH dye:

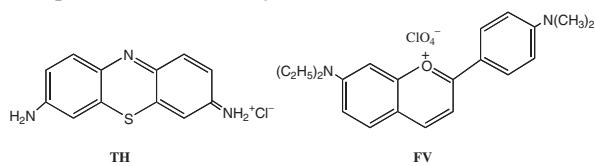


Figure 1a illustrates the color changes of protonated Nafion film doped with flavylium perchlorate (hereafter denoted as FV-Nf) upon exposure to the saturated alcohol vapors at room temperature.

The color changes took place rapidly (in 2–3 seconds), as compared with those of FV-doped sugar gel films (over 2–3 minutes).^{18,19} Exposures to many other volatile organic com-

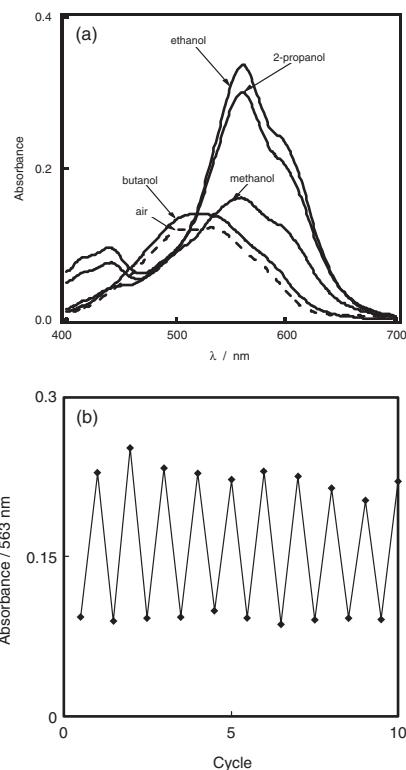


Figure 1. Vapochromism of FV-Nf film upon exposure to the saturated alcohol vapors (a), and the reversibility toward repeated alternate exposures to ethanol vapor and air (b).

pounds (VOCs) revealed rather small vapochromic responses. When the air-dried Nafion film (broken curve in Figure 1a) was further dried over anhydrous calcium chloride in a sealed cell for 24 h, the absorption band was only slightly increased. The film showed very slight spectral changes upon exposure to water vapor. Thus, the FV-Nf film revealed a low sensitivity toward humidity, and yet it revealed high sensitivities toward methanol, ethanol and 2-propanol, showing strongly structure-dependent responses. The vapochromic reversibility has been examined toward the repeated cycles of alternate exposures to ethanol vapor and air at room temperature. Figure 1b illustrates a good reversibility toward 10 repeated cycles.

It seemed interesting to further examine the vapochromic behaviors of Nafion film doped with similar cationic dyes. Thus, protonated thin film of Nafion doped with thionine (TH-Nf) was prepared by similar method. As illustrated in Figure 2, TH-Nf film revealed rather complex and varied vapochromic responses toward VOCs. The color changes took place rapidly (in 2–3 seconds). The strong band around 680 nm has been assigned to the

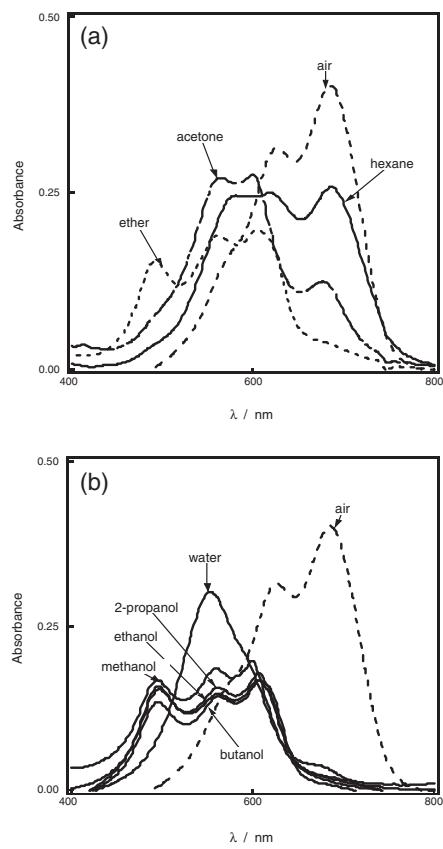


Figure 2. Vapochromism of TH-Nf film upon exposure to aprotic (a) and protic (b) vapors.

protonated dicationic species (TH_2^{2+}) of the thionine dye and the band around 600 nm to the monomeric species (TH^+), while the 550–580 nm bands to the dimeric and/or aggregates (TH^+)₂.^{20,21} Some VOCs such as hexane, acetone and ether revealed varied and extensive spectral changes as illustrated in Figure 2a, whereas benzene, toluene, acetonitrile, chloroform and ethyl acetate vapors revealed only slight spectral changes (data not shown). While exposures to methanol, ethanol, 2-propanol and butanol vapors resulted in the similar spectral changes, exposure to water vapor gave a different band around 560 nm characteristic of the thionine dimer (Figure 2b). This implies that water and alcohol vapors may cause to form different types of aggregates. The TH-Nf film revealed good vapochromic reversibilities toward the repeated exposures. Thus, after 10 repeated exposures to methanol and water vapors the absorbances around 680 nm were retained in 89 and 93%, respectively, relative to the initial ones.

The rapid color changes of the Nf film are ascribable partly to a much thinner thickness of the film as compared with those of the sugar gel films. The bathochromic shifts of the FV-Nf film shown in Figure 1a are ascribable to the dissociation of higher aggregates of FV dyes into lower aggregates and/or monomeric species (the monomer band of FV appears around 600 nm in dilute solution). Thus, the vapors permeated through the film are assumed to solvate and stabilize the dye molecules, eventually enhancing

deaggregation. In the case of TH-Nf film (Figure 2), on the other hand, the strong 680 nm band of the protonated dicationic species of thionine (TH_2^{2+}), was substantially reduced by the vapors. This is ascribable to proton transfer from the dicationic species TH_2^{2+} to the permeated vapor molecules as proton acceptors (alcohols and ether etc., but not hexane which is not a proton acceptor). However, the monomer band of TH^+ around 630 nm did not increase, but the bands around 500–600 nm increased. This implies rapid aggregation of the TH^+ species. The TH-Nf films featured rather poor thermostability, and their colors became darken upon standing for 3 weeks at room temperature, whereas the FV-Nf films retained their colors without darkening for over a month. We believe that essentially any other aggregative cationic dyes will exhibit similar vapochromic behaviors toward VOCs.

References

- 1 C. L. Exstrom, J. R. Sowa, C. A. Daws, D. Janzen, and K. R. Mann, *Chem. Mater.*, **7**, 15 (1995).
- 2 C. A. Daws, C. L. Exstrom, J. R. Sowa, and K. R. Mann, *Chem. Mater.*, **9**, 363 (1997).
- 3 J. K. Evju and K. R. Mann, *Chem. Mater.*, **11**, 1425 (1999).
- 4 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling, and R. Eisenberg, *J. Am. Chem. Soc.*, **120**, 1329 (1998).
- 5 C. E. Buss, C. E. Anderson, M. K. Pomijie, C. M. Luts, D. Britton, and K. R. Mann, *J. Am. Chem. Soc.*, **120**, 7783 (1998).
- 6 N. A. Rakow and K. S. Suslick, *Nature*, **406**, 710 (2000).
- 7 K. Okuyama, M. Ikeda, S. Yokoyama, Y. Ochiai, Y. Hamada, and M. Shimomura, *Chem. Lett.*, **1988**, 1013.
- 8 T. Seki, T. Fukuchi, and K. Ichimura, *Langmuir*, **16**, 3564 (2000).
- 9 L. Daehne, J. Tao, and G. Mao, *Langmuir*, **14**, 565 (1998).
- 10 Y. Sadaoka, Y. Sasaki, and M. Yamada, *J. Mater. Chem.*, **3**, 877 (1993).
- 11 K. Yoshida, Y. Ooyama, S. Tanikawa, and S. Watanabe, *Chem. Lett.*, **2000**, 714.
- 12 N. Nakashima and T. Kunitake, *J. Am. Chem. Soc.*, **104**, 4261 (1982).
- 13 E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara, and K. Fukuda, *Thin Solid Films*, **133**, 21 (1985); E. Ando, J. Hibino, T. Hashida, and K. Morimoto, *Thin Solid Films*, **160**, 279 (1988).
- 14 T. Seki and K. Ichimura, *J. Phys. Chem.*, **94**, 3769 (1990).
- 15 N. DiCesare, M. Belletete, C. Marrano, M. Leclerc, and G. Durocher, *J. Phys. Chem.*, **103**, 795 (1999).
- 16 M. Wang, G. L. Silva, and B. A. Armitage, *J. Am. Chem. Soc.*, **122**, 9979 (2000).
- 17 S. Zeena and K. G. Thomas, *J. Am. Chem. Soc.*, **123**, 7859 (2001).
- 18 R. Matsushima, A. Ogiue, and Y. Kohno, *Chem. Lett.*, **2002**, 436.
- 19 Presented at the Annual Meeting on Photochemistry, Kyoto, September 2002, Abstr., p 65.
- 20 S. Hamai, *Bull. Chem. Soc. Jpn.*, **73**, 861 (2000).
- 21 S. A. John and R. Ramaraj, *J. Appl. Polym. Sci.*, **65**, 777 (1997).