

Detection of Ethanol in Alcoholic Beverages or Vapor Phase Using Fluorescent Molecules Embedded in a Nanofibrous Polymer

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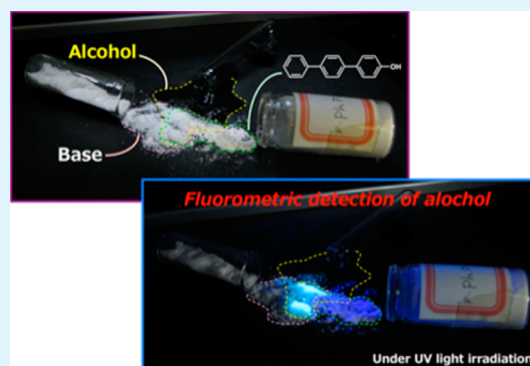
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Supporting Information

ABSTRACT: An alcohol sensor was developed using the solid-state fluorescence emission of terphenyl-ol (TPhOH) derivatives. Admixtures of TPhOH and sodium carbonate exhibited bright sky-blue fluorescence in the solid state upon addition of small quantities of ethanol. A series of terphenol derivatives was synthesized, and the effects of solvent polarities and the structures of these π -conjugated systems on their fluorescence were systematically investigated by using fluorescence spectroscopy. In particular, π -extended TPhOHs and TPhOHs containing electron-withdrawing groups exhibited significant solvatochromism, and fluorescence colors varied from blue to red. Detection of ethanol contents in alcoholic beverages (detection limit ~ 5 v/v %) was demonstrated using different TPhOHs revealing the effect of molecular structure on sensing properties. Ethanol contents in alcoholic beverages could be estimated from the intensity of the fluorescence elicited from the TPhOHs. Moreover, when terphenol and Na_2CO_3 were combined with a water-absorbent polymer, ethanol could be detected at lower concentrations. Detection of ethanol vapor (8 v/v % in air) was also accomplished using a nanofibrous polymer scaffold as the immobilized sensing film.

KEYWORDS: alcohol, phenol, fluorometric detection, composite, nanofiber



1. INTRODUCTION

Electronic tongues^{1–3} and noses^{4,5} that operate analogously with the senses of taste and smell have⁶ attracted the attention of researchers not only as a means of mimicking those human senses but also for potential applications in analyses of foods and beverages.^{7–9} On the other hand, molecule-based sensors have been developed because they present several advantages, including in the miniaturization of sensor systems and because of their excellent selectivity and tunable properties. Indeed, operation of the senses of taste and smell in higher organisms is based on the molecule-level detection of substances. Some examples of optical molecular sensors that imitate the senses of taste and smell have already been reported.^{10–19} Apart from those, detection of analytes is also undertaken using highly sensitive instrumental techniques, including gas chromatography (GC)²⁰ or infrared spectroscopy (IR).²¹

Certain phenol derivatives are known to exhibit increases in fluorescence intensity in the solid state when treated with solutions of basic substances.²² On the basis of this phenomenon, we have developed a sensor for cesium cations, which can be used to visualize cesium cations in the solid state and also in plants.^{23,24} These materials also exhibit variations in the fluorescence emission wavelength based on their overall state of protonation allowing the development of a molecular memory in solutions of organic solvents and in organogelatinous states.²⁵ In this work, we have used the solid-state fluorescence response of phenol derivatives to develop an optical sensor for the ethanol contents of various alcoholic

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beverages. Alcohol sensing has previously been achieved by colorimetric detection involving reduction of chromates or using semiconductor devices.²⁶ Also, standard techniques for alcohol detection involve GC²⁰ or IR²¹ spectroscopy. However, these systems have some disadvantages such as nonreversible detection or the requirement for the use of special and/or costly devices. A few molecule-based alcohol sensors have been reported.^{27–29} For example, Kessler et al. developed a colorimetric alcohol sensor using a solvatochromic dye.²⁸

On the basis of the latter colorimetric and solvatochromic behavior, we commenced our attempts to produce a low cost, easy to implement alcohol/ethanol sensor. Previously, we have reported that ground powdered combinations of 1 wt % TPhOH derivatives and a carbonate salt exhibit bright fluorescence (e.g., sky-blue) in the presence of ethanol under UV light irradiation.^{23,24} On the basis of this observation, we have developed a fluorometric solvent sensing system by using the phenol–phenoxide equilibrium. In particular, by introducing a substituent to the TPhOH structure, its affinity for ethanol may be increased, resulting in enhancement of its fluorescence response to ethanol. A series of phenol derivatives was synthesized, and the effects of solvents on their solid-state fluorescence emission were examined in the presence of alkali metal carbonates. The fluorescence responses of derivatives of **3** could be used to estimate ethanol contents in alcoholic beverages. Alcohol sensing for low concentrations of alcohol (for instance, contained in a “low alcohol” beer) was also attempted by combining a water-absorbent polymer with **3**. Finally, the detection of vapor phase ethanol was conducted using a nanofiber film containing **3** and a base. Our alcohol sensing system is based on visualization by fluorescence, possesses excellent reversibility and operates over a wide range of alcohol concentrations relevant to ethanol sensing in alcoholic beverages.

2. EXPERIMENTAL SECTION

2.1. General Procedures. Solvents and reagents, including phenol derivatives **1** and **2**, were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) or Wako Pure Chemical Co. (Osaka, Japan) and were used without further purification. All reactions and fractions eluted during chromatographic separations were monitored using thin layer chromatography on glass-backed plates (Kieselgel 60 F254). Developed thin layer chromatography plates were observed under UV light at 254 and 365 nm. Flash column chromatography over silica gel (LC60A35-70 μ M) was used for all separations.

2.2. Measurements. ¹H and ¹³C NMR spectra were measured at 298 K from acetone-*d*₆ solutions of the samples using a JEOL model AL300BX (300 MHz) spectrometer with SiMe₄ as the internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in parts per million (ppm) and Hertz (Hz), respectively. Electrospray ionization (ESI)-MS spectra were measured using a JASCO model JMS-T100CS. HRMS (ESI-negative) spectra were measured using a JEOL model JMS-MS700. UV/vis absorption spectra were measured using a Shimadzu model UV-3600 UV–vis-NIR spectrometer. Fluorescence spectra of solutions were measured using a JASCO model FP-6500 fluorescence spectrometer. Fluorescence spectra of solid-state samples were measured from solid samples using an Otsuka Electronics model MCPD-7000 spectrometer. Absolute quantum yield measurements were conducted using a C9920-02 instrument (Hamamatsu Photonics). Scanning electron microscopy (SEM) images were obtained using an Hitachi SU-8000 scanning electron microscope operating at an accelerating voltage of 5 kV.

2.3. Synthesis and Structural Characterization. **3**,²² **3TEG**,⁸ **4**²² and **5**³ were prepared as has been previously reported. **3F** was prepared by a literature method involving a phosphine-free Suzuki coupling reaction.³⁰

4′-(Trifluoromethyl)-[1,1′:4′,1′′-terphenyl]-4-ol (3F). A mixture of Na₂CO₃ (0.212 g, 2.0 mmol), Pd(OAc)₂ (0.001 g, 0.5 mol %), 4-bromo-4′-hydroxybiphenyl (0.249 g, 1.0 mmol), 4-(trifluoromethyl)phenylboronic acid (0.227 g, 1.2 mmol), distilled water (10 mL) and acetone (8.5 mL) was stirred for 3 h at room temperature. The resulting mixture was neutralized with dilute aqueous HCl, and the precipitate was filtered and washed with water. The residue was subjected to column chromatography (SiO₂, AcOEt) yielding **3F** as a white powder (0.234 g) in 74% yield. ¹H NMR (300 MHz, acetone-*d*₆, δ , ppm): 6.97 (d, 2H, *J* = 9.0; Ar–H), 7.60 (d, 2H, *J* = 9.0; Ar–H), 7.69–7.87 (m, 6H; Ar–H), 7.94 (d, 2H, *J* = 9.0; Ar–H), 8.55 (s, 1H; phenol–OH). ¹³C NMR (75 MHz, acetone-*d*₆, δ , ppm): 116.68, 126.53, 126.59, 126.64, 126.69, 127.72, 128.15, 128.40, 128.84, 132.22, 138.08, 141.82, 158.35. HRMS (ESI) *m/z* calcd for C₁₉H₁₂F₃O [M – H][–]: 313.084. Found: 313.082.

2.4. Alcohol Detection Procedure. TPhOH (1 wt %) derivatives (**1–5**, **3F** and **3TEG**) were mixed with a carbonate salt (Na₂CO₃ or K₂CO₃) as the matrix. The composite powder (ca. 5 mg) was placed on a substrate, and then aqueous ethanol solution, organic solvent or alcohol beverage (10 μ L) were added individually. Resulting fluorescence response was observed or a fluorescence emission spectrum was measured.

2.5. Preparation of the Composite Nanofiber Film. 1 wt% of **3** and K₂CO₃ was combined with 10 wt % aqueous poly(vinyl alcohol), and the mixture was filled into a glass syringe. The solution was forced from the syringe onto a rotating tubular substrate with application of an electrical field between the syringe needle and the substrate. A self-standing film was obtained after peeling from the substrate.

3. RESULTS AND DISCUSSION

Compound **3** exhibits weak dark-blue fluorescence in the solid state and in the presence of ethanol (added by dropping on the solid; Figure 1a). On the other hand, a ground mixture of **3** and

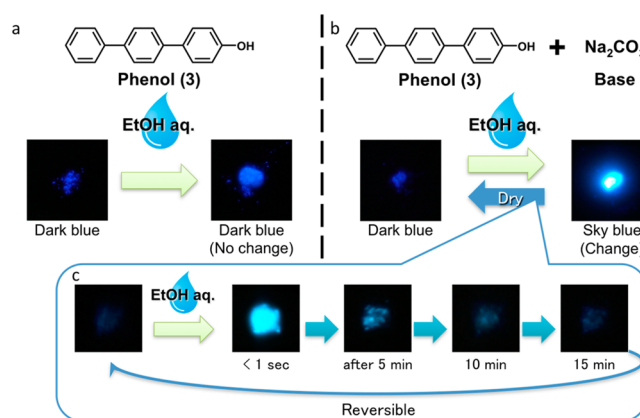


Figure 1. Color changes in the solid-state fluorescence of phenol derivatives, **3**: (a) a mixture **3** + Na₂CO₃ (b, c) under UV irradiation (365 nm) before and after addition of a drop of ethanol.

an inorganic base (Na₂CO₃) undergoes a change in the wavelength of fluorescence with a concomitant increase in the apparent emission intensity from weak dark-blue fluorescence (380 nm) to bright sky-blue fluorescence (472 nm) upon addition of ethanol (Figures 1b and S1, Supporting Information). Furthermore, the fluorescence gradually recovers to its initial weak dark-blue state with evaporation of the ethanol over a 15 min period (Figure 1c). This reversible fluorescence switching on addition of ethanol could be repetitively cycled (Figure S1, Supporting Information).

To tune the fluorescence properties of TPhOHs, other phenols prepared here were also mixed with inorganic base, and the fluorescence response was examined. Composite powders

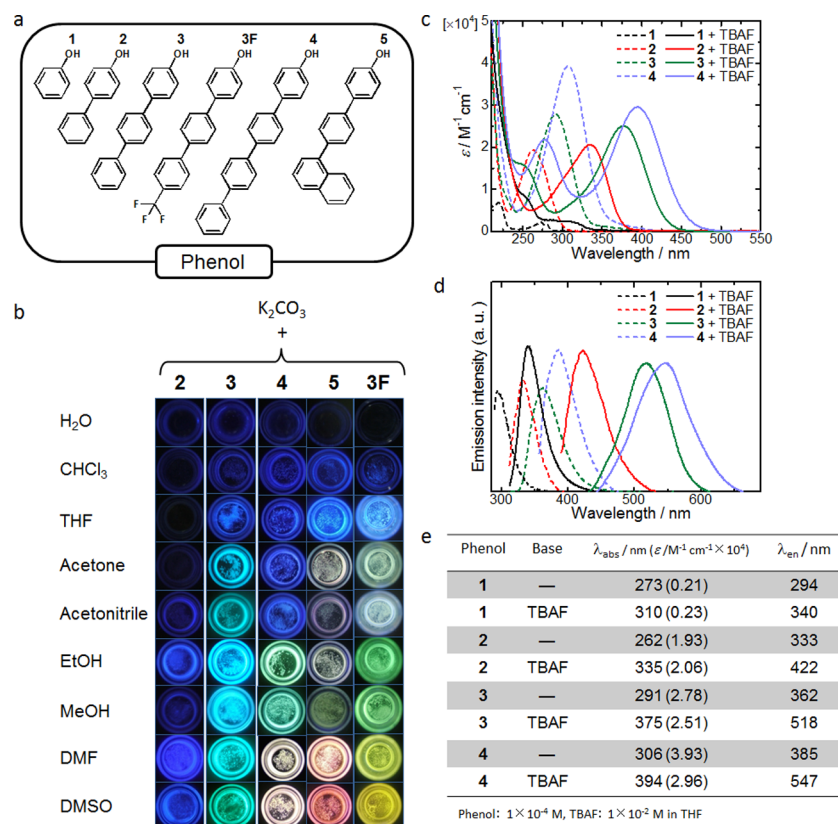


Figure 2. Color variation in the solid-state fluorescence of phenol derivatives in the presence of base and various organic solvents. (a) Chemical structures of the phenol 1, 2, 3, 3F, 4, 5. (b) Photographs of combinations of phenol (2, 3, 4, 5, 3F) and K_2CO_3 under UV irradiation (365 nm) after addition of different solvents. UV/vis (c) and fluorescence (d) spectra of phenols 1 to 4 in THF (1.0×10^{-4} M) before and after addition of TBAF in THF (1.0×10^{-2} M). Data is summarized in the table (e).

of the phenol derivatives (2–5, 3F) and base (K_2CO_3) were prepared by grinding, and variation in the fluorescence of these powders was examined after addition of different organic solvents (water, chloroform, tetrahydrofuran (THF), acetone, acetonitrile, ethanol, methanol, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) (Figures 2 and S2, Supporting Information), revealing that fluorescence color of 3 varies from blue to green depending on the solvent. The other phenols also showed solvatochromism in their fluorescence (4, blue-white; 5, blue-pink; 3F, blue-yellow). Interestingly, 3F showed white-colored emission only in the presence of acetonitrile, suggesting its use as a selective sensor for that solvent. The chromaticity coordinates calculated from the fluorescence spectrum of 3F are at (0.32, 0.38), which is located nearly in the white region according to the 1934 CIE coordinate diagram. Comparison of 4 and 5 with 3 revealed a more significant solvatochromism over 3 probably because of the increased extent of their π -conjugated systems. Calculation of the molecular orbital structures suggests that the phenoxide form of 3F undergoes intramolecular electron transfer in its excited state (Figure S3, Supporting Information). This in turn suggests that trifluoromethyl units in the structure of 3F decrease the electron density at the terminal phenyl group and enhance intramolecular electron transfer. Thus, 3F exhibits fluorescence at longer wavelengths than 3. Maximum fluorescence wavelengths were plotted against $E_{\text{T}}(30)$ values,³¹ which denote the polarity characteristics of each organic solvent (Figure S4, Supporting Information). In these plots, the points for solvents of higher polarity show reasonable linearity. The

discontinuity for solvents of higher polarity is likely due to the effects of hydrogen bonding between the phenol and solvent molecules. In addition, significant red shifts were observed in fluorescence and UV/vis absorption bands of phenols (50–160 nm) upon addition of basic (tetra-*n*-butylammonium fluoride: TBAF) even in THF solutions. (Figure 2c,d,e) It should be noted that the phenols 3 and 3F give a very similar response for ethanol and methanol. However, in our subsequent development of ethanol sensing systems, it should be noted that methanol and ethanol can also be differentiated colorimetrically using another dye system developed in our laboratory.³² However, to develop a sensor suitable for dual sensing and differentiation of ethanol and methanol, it would be necessary to identify an appropriate nanolamellar medium that fulfills the requirements of dimensions (to accommodate large dye chromophores) and basicity (to enhance the fluorescence response).

Solid-state fluorescence responses of the phenols in admixture with carbonate were applied for ethanol sensing. After adding a series of aqueous ethanol solutions to 3 or 3TEG in the solid state in admixture with Na_2CO_3 , absolute quantum yields were measured (Figure 3a,b). Here, the value of absolute quantum yield is treated as a quantitative fluorescence intensity of the solid-state sample. With increasing ethanol content, fluorescence intensity increased and gave sigmoidal-shaped curves when plotted against the water/ethanol ratio. This indicates that the fluorescence response is closely related to deprotonation of the phenol. 3TEG showed stronger fluorescence than 3, and the detection limit was ca. 15 v/v %

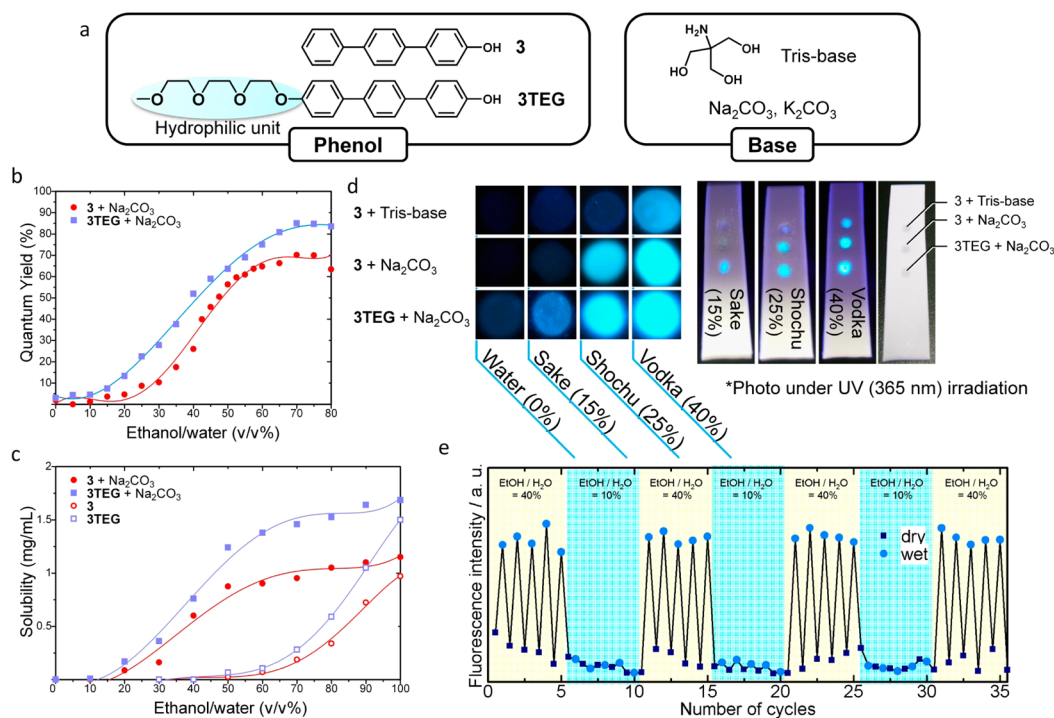


Figure 3. Ethanol concentration response of mixtures of phenol derivatives and a base. (a) Chemical structures of the phenol derivatives and bases used. (b) Variation in quantum yields of the mixtures $3 + \text{Na}_2\text{CO}_3$ and $3\text{TEG} + \text{Na}_2\text{CO}_3$ in ethanol/water with concentration. (c) Solubility dependencies of phenol **3** and **3TEG**, and their admixtures $3 + \text{Na}_2\text{CO}_3$ and $3\text{TEG} + \text{Na}_2\text{CO}_3$ based on ethanol/water ratio. (d) Photographs of the admixtures $3 + \text{Tris}$, $3 + \text{Na}_2\text{CO}_3$, and $3\text{TEG} + \text{Na}_2\text{CO}_3$ under UV irradiation (365 nm) after dropping various alcoholic beverages of differing ethanol contents. (e) Reversible switching of fluorescence intensities of the mixture $3 + \text{Na}_2\text{CO}_3$ with alternation between 40% and 10% ethanol/water (v/v) mixtures.

of ethanol (3: 30 v/v %). To examine this behavior, solubilities of **3** or **3TEG** (in admixture with sodium carbonate) in a series of aqueous ethanol solutions were also measured. Variations in solubility gave similarly sigmoidal-shaped curves as those obtained for quantum yields (Figure 3c). Thus, it seems likely that the fluorescence response is due to dissolution of the phenol and base in the aqueous ethanol solution probably with concomitant reaction to the deprotonated more highly fluorescent phenoxide in solution. Thus, the solubility of the phenols in the presence of base is a key factor in the fluorescence response in ethanol/water. Consequently, because the more hydrophilic phenol **3TEG** is more soluble in solvent mixtures of low alcohol concentration, it showed improved sensitivity over TPhOH **3**. We also attempted ethanol sensing in alcoholic beverages (Figure 3d). As expected, a brighter fluorescence response was observed for those with increasing ethanol contents. An ethanol sensor array involving a series of phenols (**3** and **3F**) and bases (triethylamine, Na_2CO_3 and K_2CO_3) enabled estimation of the alcoholic beverages simply by observing differences in fluorescence intensity. In addition, the same sensor array could be repetitively applied for ethanol content sensing simply by drying between analyses (Figure 3e). Ethanol contents could be estimated in the range from 5–70 v/v % and, in addition, the approximate linearity of the fluorescence quantum yield plot between 25 and 75 v/v % might also be used to estimate ethanol content.

We found that including a water-absorbent polymer led to an enhanced sensitivity for this system (Figure 4a), presumably due to an increase in the local ethanol:water ratio. Solid **3** and Na_2CO_3 were mixed and combined with sodium polyacrylate as

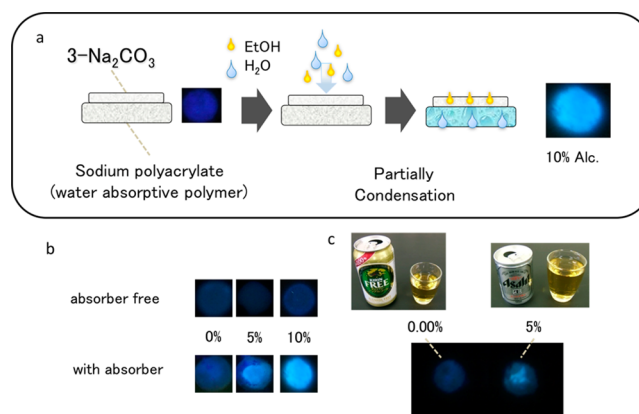


Figure 4. Improving ethanol concentration sensitivity of the admixtures of phenol derivatives and base by incorporation in a water absorbent polymer. (a) Schematic illustration of $3 + \text{Na}_2\text{CO}_3$ on sodium polyacrylate to estimate lower alcohol concentrations. Photographs of $3 + \text{Na}_2\text{CO}_3$ on sodium polyacrylate after dropping wine (~10% Alc.) under UV irradiation (365 nm). (b) Fluorescence changes for the mixture $3 + \text{Na}_2\text{CO}_3$ on sodium polyacrylate after dropping various alcoholic beverages (of the indicated ethanol concentrations) under UV irradiation (365 nm). (c) Photographs of $3 + \text{Na}_2\text{CO}_3$ on sodium polyacrylate under UV irradiation (365 nm) after dropping nonalcoholic beer (left) and normal beer (right).

the water-absorbent polymer. In this case, the sensor material could be used to detect down to 5 v/v % of ethanol in water by observing the fluorescence response (Figure 4b). The polymer layer absorbs water from the alcohol mixture thereby increasing the ethanol content and facilitating its detection. By this means, sensing of ethanol in beer (5 v/v %) could be demonstrated

although ethanol content of nonalcoholic beer could not be estimated (Figure 4c). Thus, the sensitivity of solid-state detection using fluorescence was improved to 5 v/v % ethanol content by incorporating the probe molecules (and base) into a water-absorbent polymer, and the ethanol contents of commercially available alcoholic beverages could be estimated.

Sensing of ethanol in the vapor phase was also attempted by incorporating the phenol/base system with other materials. **3** and Na₂CO₃ were mixed with basic alumina (basic Al₂O₃) and the characteristic bright sky-blue fluorescence could easily be observed under a flow of ethanol-saturated air, although a solid mixture of **3** and Na₂CO₃ without basic Al₂O₃ showed no observable fluorescence under similar treatment (Figure 5b).

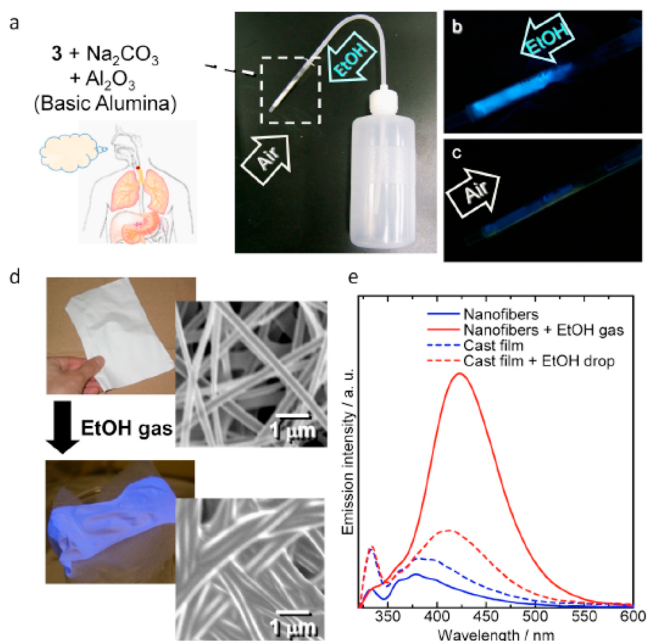


Figure 5. Ethanol vapor sensing involving phenol/base composite nanofibers. (a) Photograph of ethanol vapor sensor prepared from **3** + Na₂CO₃ and basic alumina contained in a plastic tube. (b and c) Fluorescence variation of ethanol vapor sensor under UV irradiation (365 nm) with ethanol vapor (b) and air (c) passing through. (d) Composite nanofiber film prepared by electrospinning of an aqueous solution containing **3**, K₂CO₃ and PVA. Photographs of the free-standing composite nanofiber film under normal light (top left, d) and following exposure to ethanol vapor under UV irradiation (365 nm) (bottom left, d). SEM images of composite nanofiber film before (top right, d) and after exposure to ethanol vapor (bottom right, d). (e) Fluorescence spectra of composite nanofiber film and cast films prepared from an aqueous solution of **3**, K₂CO₃ and PVA, before and after exposure to ethanol vapor.

Fluorescence due to the ethanol vapor was eliminated by flowing ethanol-free air; a sensing process that could be repeated many times (Figure 5c). We suppose that the response to ethanol vapor is enhanced in this case since basic alumina increases the prevalence of the phenoxide form over that simply in the presence of sodium carbonate. Basic alumina was used because of its basicity and the use of other common media available in our laboratory at the time (i.e., neutral alumina, silica (acidic)) did not yield any fluorescence enhancement when applied in this way. We also attempted to further improve sensitivity toward vapor phase ethanol by increasing the available surface area for sensing. For this

purpose, we prepared a PVA nanofiber film as a composite containing **3** and K₂CO₃ by using the electrospinning technique. The material obtained was a self-standing film with an internal structure of high surface area composed of entangled nanoscale fibers observed by scanning electron microscopy (SEM) (Figure 5d). A clear fluorescence response was observed in the nanofiber film when placed in a flow of ethanol-saturated air. Fluorescence emission measurements revealed that this film gave a 10-fold enhancement of fluorescence emission intensity over a cast film (Figure 5e), leading to greater sensitivity to ethanol vapor.

The use of colorimetric or fluorometric tests^{22–29} has the advantages of simple implementation and applicability by untrained personnel. Of course, instrumental techniques^{20,21} provide excellent accuracy but can be expensive and are inconvenient especially when only a rapid estimation of alcohol content (or simply the presence) is required. Therefore, the method presented here does present some advantages for on-the-spot testing of an analyte. After optimization or adaptation, this advantage would allow field testing of samples such as illicitly produced alcohol-containing liquors or adulterated petrochemical products, or estimations of the ethanol content of those materials. In the field testing would most appropriately be followed by laboratory determinations of the analytes but the rapid estimation could be a valuable tool.

4. CONCLUSION

In summary, we have developed an alcohol sensor involving solid-state fluorescence emission of phenol derivatives. Combinations of compounds **3** or **3TEG** with carbonate in the solid state can be used to estimate ethanol contents in alcoholic beverages due to a bright fluorescence emission in the presence of concentrated ethanol (more than 15 v/v %) solutions. Sensitivity could be improved by incorporation of the sensing material into a water-absorbent polymer leading to estimation of ethanol contents in solution down to 5 v/v % by simple observation of fluorescence. In addition, combining the ethanol sensor in a nanofiber polymer film possessing a large surface area enabled detection of ethanol in the vapor phase. We note that, despite being able to improve the sensitivity of our system by various means, it still does not approach the precision or accuracy of the methods currently used. Also, as mentioned previously, it is a simple matter to combine the sensing activity reported here with that of other colorimetric or fluorometric systems especially in order to differentiate ethanol from other related analytes such as methanol. We have already achieved the latter²⁸ and, with that in hand, we are currently working to combine ethanol sensing and differentiation in a single sensing system. In particular, using synthetic methods, we are developing novel fluorescent molecules in order to improve the accuracy and sensitivity of our present method. With that in mind, an appropriate combination of fluorescent dyes might be developed that, when implemented as paper or polymer strips, could be used to provide information on the ethanol content (or that of other analytes) in a sample. In terms of applicability, we believe that such a system would be of assistance to any personnel requiring an on-the-spot estimation of ethanol content.

■ ASSOCIATED CONTENT

Supporting Information

Fluorescence spectra, a cycle test of the detection, fluorescence wavelengths of several phenol derivatives and their plots against

$E_T(30)$ values, additional fluorescence spectra and quantum yield data. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Accession Codes

1 (100-95-2); 2 (92-69-3); 3 (13041-65-1); 4 (126842-06-6); 5 (1639875-92-5).

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Author Contributions

M. Akamatsu, T.M. and K.O. performed most of the experiments. K.K. and S.S. fabricated and characterized the composite nanofiber film. M.Y. and T.N. performed absolute fluorescence quantum yield measurements. H.S., M. Abe, J.P.H. and K.A. conceived the project. M. Akamatsu and H.K. wrote the paper. The paper was written with contributions from all the authors.

Notes

The authors declare no competing financial interest.

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