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Discrimination of Methanol from Ethanol in Gasoline Using a Membrane-type Surface Stress Sensor Coated with Copper(I) Complex#

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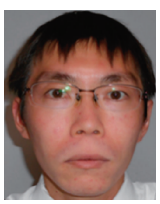

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Abstract

We successfully fabricated a novel sensing platform, a Membrane-type Surface stress Sensor (MSS) coated with copper(I) complex bearing phen and BINAP ligands, [Cu(phen)((±)-BINAP)]PF_6 (**1**, phen = 1,10-phenanthroline, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), for specific molecular sensing. Based on the transduction of mechanical stresses derived from sorption-induced deformation of Cu(I) complex, the detection performance of various volatile organic compounds (VOCs) has been investigated. The fabricated sensor devices showed selective responses to methanol over a wide range of VOCs. In addition, distinct MSS signals upon exposure to methanol were observed for mixing samples of methanol in *n*-hexane and gasoline with clear discrimination of ethanol mixtures. In fact, gasoline vapor with 1% methanol exhibited much higher MSS responses than 20% ethanol containing gasoline samples. Methanol contamination in gasoline and related petroleum samples is a world-wide common problem in the automobile and fuel sectors where detection of methanol contaminants with portable devices by easy procedures is required. The current research results will contribute to fulfilling these social demands.

Keywords: Membrane-type Surface stress Sensor (MSS) | Copper(I) complex | Methanol fuel

1. Introduction

One of the crucial demands in current society is a development of sensing systems for the detection and removal of environmental risks and biological dangers with simple and inexpensive procedures.[1–3] For example, illegal usages of methanol in alcoholic beverages and gasoline as fake-ethanol have to be instantly detected to avoid serious health problems and automobile damage, respectively. However, the rather featureless nature of methanol and its characteristic resemblance to ethanol make methanol sensing unexpectedly difficult. Although the discrimination between methanol and ethanol can be analyzed by proper analytical instrumentation (e.g. gas chromatography-mass spectrometry, NMR), facile and selective detection of methanol is still a challenging subject among various sensing demands.

Various research efforts on methanol sensing and related matters have been actively made and been reported.[4–16] For example, Ishihara et al. reported the colorimetric discrimination of methanol from ethanol using a composite film based on porphyrin-type dye (oxoporphyrinogen) and layered double hydroxide.[4] Because of the visible color change upon methanol exposure, the composite films can be applied as low-cost and portable colorimetric sensing systems for methanol in gasoline.[4,5] The other promising approach to methanol sensing is Raman-based sensors.[7–9] The characteristic Raman signal of methanol can be discriminated from gasoline,[8] leading to the detection of methanol in gasoline. However, the sensing devices of methanol from mixtures such as gasoline using repeatable and mobile systems are still limited, preventing a practical implementation of the methanol sensors. Facile detection systems with high sensitivity for methanol in gasoline or high ethanol content samples are awaited to be explored.

As a novel sensing system for versatile usages, we have recently developed a new type of static mode nanomechanical sensor—Membrane-type Surface stress Sensor (MSS). The MSS is composed of a silicon-based membrane suspended by four piezoresistive sensing beams, composing a full Wheatstone bridge, achieving high sensitivity with compactness.[17,18] The MSS exhibits higher repeatability than a conventional cantilever-type nanomechanical sensor, due to the high robustness.[19,20] The MSS transduces surface stresses derived from the absorption/desorption-induced deformation (i.e. swelling or shrinking) of a receptor layer coated on the membrane. Therefore, any kind of interaction between target molecules and the receptor materials accompanied by mechanical deformation is potentially detected by the MSS. Among various candidates of sensing materials, the selectivity can be tuned by appropriate fabrication of sensing materials,[21–30] while it is still limited to fabricate the sensing materials, which have high sensitivity to methanol, distinguishing methanol and ethanol.[22,30] In the present paper, we have found that Cu(I) complex bearing diimine and diphosphine ligands have a high capability for selective sensing of methanol.

Cu(I) complexes bearing diimine and diphosphine ligands from a cheap abundant metal source are promising metal complexes for many applications such as photoredox reactions,[31–33] light emitting devices,[34] and luminescence sensors for oxy-

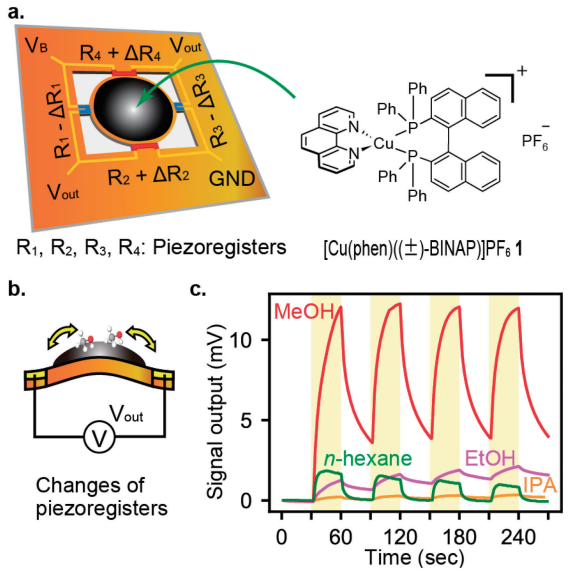

Figure 1. Membrane-type Surface stress Sensor (MSS) coated with copper(I) complex **1**. (a) The schematic illustrations of the configuration of MSS and the structure of Cu(I) complex bearing phen and BINAP ligands, [Cu(phen)((±)-BINAP)]PF_6 **1** (phen = 1,10-phenanthroline, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl). (b) Working principle of the detection of gases using the MSS. (c) Typical signal outputs of Cu(I) complex-coated MSS for various VOCs.

gen.[35] However, the fabrication of electric sensors based on solid of this type of Cu(I) complex has not been fully explored. Here, we report a gas sensor, which is capable of detecting methanol contamination in gasoline, based on MSS coated with solid Cu(I) complex (Figure 1). Aiming to fabricate solid of Cu(I) complex as a receptor for MSS, we selected [Cu(phen)-((±)-BINAP)]PF_6 (**1**, phen = 1,10-phenanthroline, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl). Since the complex metal center is surrounded by hydrogen atoms in aromatic C-H bonds or fluorine atoms in PF_6 anion, weak interaction between these moieties would work for the effective absorption of methanol and the rigid and sterically hindered ligands effectively form a densely packed bulk receptor layer, which gives limited intermolecular space, leading to the discrimination of small molecules sensitively. This type of Cu(I) complex enables us to expect methanol molecule to interact with these moieties for facile and selective detection of methanol by MSS devices.

2. Experimental

2.1 Materials. Tetrakis(acetonitrile)copper(I) hexafluorophosphate ([$Cu(CH_3CN)_4$]PF_4) and 1,10-phenanthroline (phen) were purchased from Aldrich. (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((±)-BINAP) was purchased from Tokyo Chemical Industry Co. Ltd. Dichloromethane, diethyl ether, *N*,*N*-dimethylacetamide (DMA), and all deuterated solvents were purchased from Aldrich, Tokyo Chemical Industry Co. Ltd., and Wako Pure Chemical, and used as purchased. As for the sensing measurement, methanol, ethanol, 2-propanol, *n*-hexane, *n*-heptane, benzene, toluene, acetone, and ethyl acetate in analytical grades were used. Regular gasoline was purchased from ENEOS corporation. To obtain water vapor, MilliQ water was used (Merck MilliPore).

2.2 Synthesis of [Cu(phen)((±)-BINAP)]PF_6 1. [Cu(phen)((±)-BINAP)]PF_6 **1** was synthesized according to a modified procedure described in the literature.[36] [$Cu(CH_3CN)_4$]-PF_4 (186 mg, 0.500 mmol) was added to a solution of (±)-BINAP (313 mg, 0.503 mmol; 1.0 equiv.) and phen (90.2 mg, 0.501 mmol; 1.0 equiv.) in CH_2Cl_2 (7.5 mL). After stirring for 1.5 h at room temperature under air, diethyl ether (0.5 mL) was added to the reaction mixture to obtain a yellow suspension. The suspension was collected by filtration, washed with diethyl ether (2.5 mL), and dried under reduced pressure to yield [Cu(phen)((±)-BINAP)]PF_6 **1** (297 mg, 59%). ^{1}H NMR (acetone-d_6, 300.40 MHz) $\delta = 9.27$ (*d*, $J = 4.8$ Hz, 2H), 8.91 (*d*, $J = 8.1$ Hz, 2H), 8.34 (*s*, 2H), 8.13 (*dd*, $J = 4.8$, 8.1 Hz, 2H), 7.88 (*d*, $J = 8.1$ Hz, 2H), 7.76 (*d*, $J = 8.1$ Hz, 2H), 7.48–7.38 (*m*, 8H), 7.36–7.10 (*m*, 12H) 6.96 (*d*, $J = 8.0$ Hz, 2H), 6.85 (*dd*, $J = 7.8$, 7.8 Hz, 2H), 6.70 (*dd*, $J = 7.8$, 7.8 Hz, 4H) (Figure S1).

^{1}H NMR spectra were recorded with a JEOL AL300 FT-NMR spectrometer. We note that the related parent complexes, [Cu(phen)((*S*)-BINAP)]PF_6[36] are known compounds with sufficient identifications including NMR data.

2.3 Fabrication of Cu(I) Complex-Coated MSS. [Cu(phen)((±)-BINAP)]PF_6 **1** was directly coated onto the surface of the MSS by inkjet spotting using an inkjet spotter (LaboJet-500SP, Microjet Co. Ltd.) equipped with a nozzle (IJHBS-300, Microjet Co. Ltd.). [Cu(phen)((±)-BINAP)]PF_6 **1** (0.72 mg) was dissolved in 2.5 mL of DMA and then sonicated for ca. 5 min. The resulting yellow solution of **1** was loaded into the inkjet nozzle, and 300 sequential droplet depositions were performed. The inkjet stage was heated to 80 °C to control evaporation of DMA.

2.4 Sensing System and Procedure. The Cu(I) complex-coated MSS chip was loaded in a Teflon chamber placed in an incubator (HCRCSIV-A series) at a controlled temperature of 25.00 ± 0.02 °C. The chamber was connected to a gas flow system consisting of two mass flow controllers (MFCs), a mixing chamber, a purging gas line, and a vial for target sample liquid, including a single component guest and guest mixtures. The carrier nitrogen gas, which was saturated vapor with target solvent vapors, was then diluted at 20% with pure nitrogen gas by using two MFCs. The diluted vapor was introduced to the sensor for 30 sec. Four injection-purging (ON-OFF) cycles were performed and data were recorded at a sampling rate of 20 Hz by applying a bridge voltage of −0.5 V to the Wheatstone bridge. The selectivity tests were performed using 8 different vapors (i.e. water, methanol, ethanol, 2-propanol, acetone, ethyl acetate, *n*-hexane, benzene, and toluene were used in this present study). As a reference, the signal response of bare MSS to methanol was also measured (see supporting information). As the model of methanol fuel, detections of methanol were performed using the mixtures of methanol in *n*-hexane. Methanol was diluted with *n*-hexane in concentrations ranging from 0 to 100 mol%. The resulting solvent vapors were introduced to the sensor. In the actual gas sensing, 1 vol% of methanol in regular gasoline was used, and 20 vol% of ethanol in gasoline (commonly known as E20 fuel) was used as a reference.

To identify the chemical selectivity of the Cu(I) complex-coated MSS for the varieties of VOCs, we evaluated the signal intensity for each VOC extracted from the last three signal responses from 90 to 330 sec out of four signal responses in each measurement, because the latter signal responses can provide more reproducible signal responses than the former ones, which exhibit initial fluctuations associated with mixing of sample gases and pre-adsorbed gases.

3. Results and Discussion

[Cu(phen)((±)-BINAP)]PF_6 **1** was synthesized according to the modified procedure described in literature.[36] As-synthesized Cu(I) complex **1** exhibited high solubility in several organic solvents, especially polar solvents, such as chloroform, acetone, dimethylsulfoxide, and so on (Figure S1–S3).[31] The Raman spectrum of the as-synthesized solid of **1** shows obvious signals of 1209, 1299, 1342, 1375, 1422, 1450, 1511, and 1589 cm^{-1} (Figure S4). These signals in a range from 1400 to 1600 cm^{-1} can be interpreted as bands derived from the aromatic groups due to C=C or C=N bending of aromatic rings such as phenyl, binaphthyl, and diimine moieties. In the case of this type of heteroleptic Cu(I) complexes, the complex metal center is surrounded by sterically bulky aromatic ligands, preventing the reactivity of the complexes with solvent molecules.[36] We also evaluated the reactivity of **1** to methanol. The chemical shift of Cu(I) complex **1** in acetone-d_6 in the presence of methanol-d_6 was measured. As shown in Figure S5, the chemical shift of **1** in acetone-d_6–methanol-d_6 (v/v 100:1) is similar to that in acetone-d_6, indicating that the reaction of Cu(I) complex **1** to methanol is negligible at least in the solution state even in the presence of an excess amount of methanol, due to the metal center surrounded by the aromatic ligands. As the complex metal center is surrounded by hydrogen atoms in aromatic C-H bonds or fluorine atoms in PF_6 anion, weak interaction between these moieties is expected to work for discrimination of small molecules sensitively.

Chemical stability is one of the most important factors of sensing materials for practical applications. We evaluated the chemical stability of the Cu(I) complex by using ^{1}H NMR measurement. The chemical shifts of all signals of the ^{1}H NMR spectrum after dissolving the Cu(I) complex **1** in acetone-d_6 at room temperature within 1 hour are the same as those of ^{1}H NMR after 1 day and 6 days under the same conditions (Figure S1). In addition, the chemical shifts of Cu(I) complex **1** in acetone-d_6–methanol-d_6 (v/v 100:1) showed no significant changes for 8 days (Figure S5). These results indicate that the acetone solution of Cu(I) complex **1** is stable enough under air at room temperature for more than 8 days. Importantly, the powder **1**, which was kept at room temperature under air for 6 months, was dissolved in acetone-d_6 and then ^{1}H NMR measurement was performed. As shown in Figure S1, the signals are similar to as-synthesized complex **1** in acetone-d_6, indicating that the Cu(I) complex **1** in the solid phase is highly stable under ambient conditions. These results suggest that the Cu(I) complex **1** is suitable for the sensing materials of nanomechanical sensing.

We fabricated the Cu(I) complex-based MSS by inkjet spotting directly onto the membrane of the MSS. The sensing responses to the various solvent vapors are shown in Figure 2 (detailed responses are shown in Figure S6). The Cu(I) complex film effectively absorbs various solvent vapors and generates the absorption-induced deformation (see also Figure S7 for the signal response of bare MSS). The Cu(I) complex-based MSS yields significantly high intensity to methanol vapor up to 8 mV, and approximately 8–10 fold higher selectivity to methanol can be observed compared to a wide range of the other organic solvent vapors including polar (i.e. ethanol, 2-propanol, acetone, and ethyl acetate) and non-polar solvents (i.e. *n*-hexane, benzene, and toluene). It should be noted that the sensitivity of the nanomechanical sensing based on gas–solid equilibrium, including the MSS, generally depends on partial vapor pressure, which is a vapor pressure divided by the

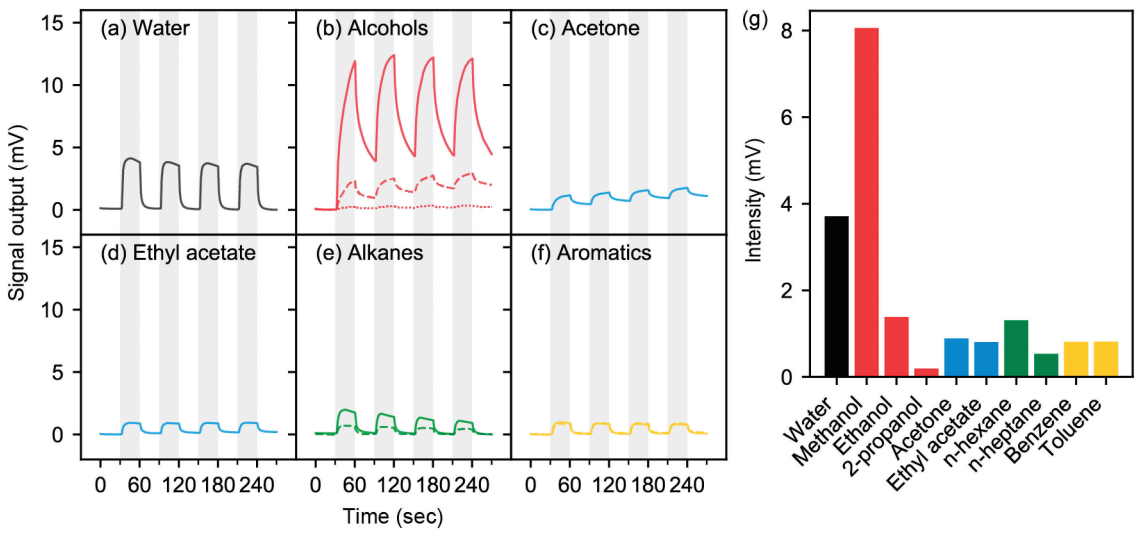

Figure 2. Responses of [Cu(phen)((±)-BINAP)]PF_6 **1** to various vapors. (a–f) Signal responses of **1** to water (a); alcohols (i.e. methanol (solid line), ethanol (dashed line), and 2-propanol (dotted line)) (b); acetone (c); ethyl acetate (d); alkanes (i.e. *n*-hexane (solid line) and *n*-heptane (dashed line)) (e); and aromatics (i.e. benzene (solid line) and toluene (dashed line)) (f). Details are shown in Figure S6. (g) Intensities of **1** to various vapors. Colors correspond to those used in (a)–(f).

saturated vapor pressure, rather than the absolute concentration of vapors.[24,37] Although 20% saturated methanol vapor (33,000 ppm) is slightly smaller than that of *n*-hexane (39,000 ppm) and is slightly higher than that of acetone (44,000 ppm) calculated by the saturated vapor pressure (Table S1),[38] the partial vapor pressure of the samples was fixed at 20% by precisely controlling the two MFCs. Thus, the specific interaction of methanol with hydrogen atoms in aromatic C–H bonds and/or fluorine atoms in PF_6^- anion of the Cu(I) complex **1** may enhance the absorption of methanol molecules in the receptor layer, leading to the superior selectivity to methanol.

Importantly, the Cu(I) complex yields high selectivity to methanol even among the series of alcohols (i.e. methanol, ethanol, and 2-propanol). Figure S8 depicts the signal intensities of VOCs including water as a function of molecular weight, which is related to the volume of each molecule. The signal intensities to the samples, whose molecular weights are higher than methanol, dramatically decreased to less than 1 mV, while the intensity to water yields relatively high intensity (3 mV) compared to the other organic vapors. This result suggests that methanol molecule is small enough to interact with the Cu(I) complex in the solid phase of the receptor layer, due to the rigid structures of aromatic ligands without any flexible functional groups (e.g. alkyl chains). Although water molecule is smaller than methanol, the sensitivity to water is lower than methanol, possibly due to the hydrophobic nature of aromatic ligands on the Cu(I) complex **1**.

With the superior selectivity of the Cu(I) complex-based MSS to methanol compared to *n*-hexane, we also examined the specific detection of methanol from the mixture of methanol and other organic solvents (i.e. *n*-hexane). The gas sensing measurements were performed using a wide range of mixtures of methanol/*n*-hexane (Figure S9). The signal intensities for the mixtures are plotted as a function of molar ratios of alcoholic contents in *n*-hexane (Figure 3). It has to be noted that the mixture of methanol and *n*-hexane with 76 mol% is obviously separated into two phases, due to the low miscibility of methanol in *n*-hexane (up to 21 mol%).[39] Since the molar ratio of methanol in the vapor phase as well as the partial pressure of methanol are almost constant in a range from 14.4 mol% (16.01 kPa) to 94.0 mol% (16.70 kPa) at 25 °C,[39] the signal intensities reached constant values over 14 mol% (ca. 6 mV). In contrast to the case of the high content of methanol in *n*-hexane, the signal intensities are drastically enhanced with linear correlation to the increase of methanol contents at the range from 1.6 mol% to 6.1 mol% (Figure 3b). This linear correlation is attributed to the increase of the concentration of methanol in the vapor phase. Indeed, the reported molar ratio of methanol and total pressure are drastically changed in a range from 0 mol% in liquid (0 mol% in vapor, 16.16 kPa), 0.8 mol% in liquid (29 mol% in vapor, 22.37 kPa), and 8.5 mol% in liquid (42 mol% in vapor, 27.50 kPa).[39] Importantly, ethanol in *n*-hexane exhibited insensitive nature over a wide range of mixing ratios. In contrast to methanol, ethanol can be freely miscible with *n*-hexane, whereas the signal intensity did not show an increase even in the high concentration of ethanol vapor (Figure 3a and Figure S10). These results clearly suggested the utility of the Cu(I) complex-based MSS for the detection of methanol in gasoline as well as the mixture of high ethanol content samples.

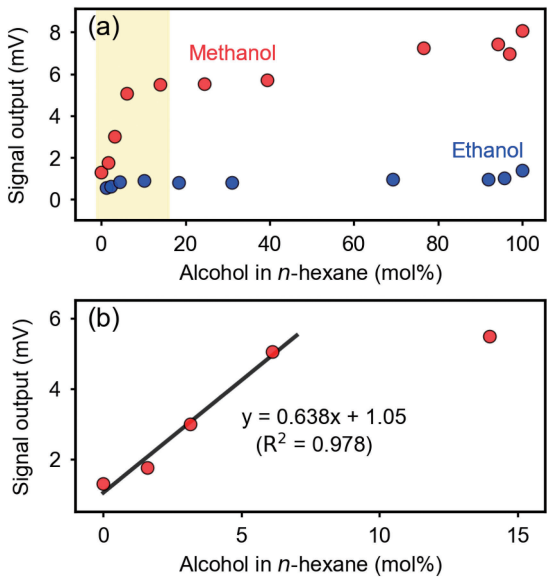

Figure 3. Selective response of Cu(I) complex **1** to methanol in *n*-hexane. (a) Intensities of **1** to methanol (red circles) and ethanol (blue circles) in *n*-hexane ranging from 0 to 100 mol%. (b) Magnified plots of methanol in *n*-hexane ranging from 0 to 15 mol%. A black line indicates the line fit with R^2 value.

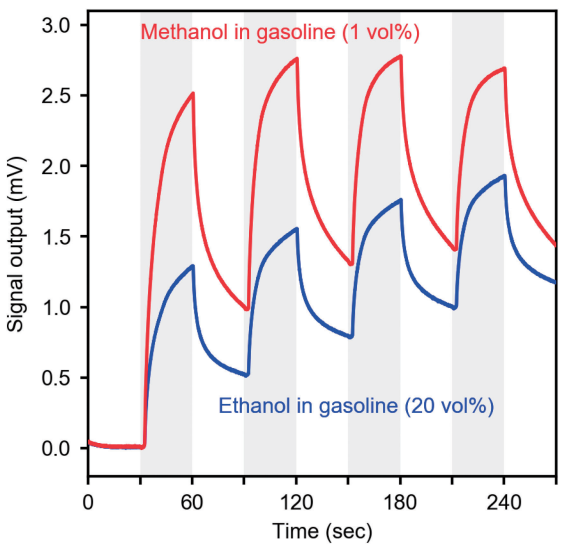

Figure 4. Detection of methanol in gasoline by Cu(I) complex-coated MSS. Red and blue lines are 1 vol% of methanol in gasoline and 20 vol% of ethanol in gasoline (the model of E20 fuel).

Finally, we have demonstrated the availability of the Cu(I) complex-coated MSS for the methanol sensing of methanol-containing gasoline. The Cu(I) complex-coated MSS was exposed to the vapor of gasoline with 1% methanol (Figure 4). The Cu(I) complex-coated MSS yielded significant sensitivity to methanol-containing gasoline as compared to the ethanol-containing gasoline, even when the ethanol content in gasoline is 20 times higher than methanol in gasoline. This result clearly indicates the efficient detection and discrimination between methanol and ethanol in gasoline are successfully achieved.

Detailed mechanisms on the superior sensitivity of the MSS coated with Cu(I) complex **1** are not fully clear. The high affinity of methanol to this Cu(I) complex would be one of the effective factors of such selective sensitivity to methanol. We speculate from the experimental facts that crystals of this type of Cu(I) complexes often include methanol molecules as a co-existing component in the crystals.[40] The results would suggest the existence of intermolecular space among the Cu(I) complex **1** in the solid phase, which may fit the size of methanol molecule. In contrast to methanol, other relatively large analytes may not penetrate into the receptor layer, resulting in the low signal responses. We note that powder XRD patterns of Cu(I) complex **1** film on glass plate are not much influenced by methanol vapor (Figure S11), suggesting that the aforementioned intermolecular space may be in amorphous and/or short-range order states.

Inappropriate contamination of expensive safe ethanol by inexpensive toxic methanol in gasoline as well as in beverages is a serious problem. Contaminated methanol in gasoline causes heavy damage to automobile engines, while that in drinks induces serious health problems. The sensor systems presented in this study would make significant contributions to safe and reliable social activities. In addition, the Cu(I) complex-based MSS yielded low sensitivity to water vapor, suggesting a highly advantageous feature for sensor usages under practical conditions, such as in the presence of moisture or humidified conditions.

4. Conclusion

We successfully evaluated the utility of heteroleptic copper(I) complex bearing phen and BINAP ligands for methanol sensing. The fabricated sensor exhibited high selectivity to methanol vapor over a wide range of VOCs. In addition, distinct signals of the Cu(I) complex MSS upon exposure to methanol were observed for mixing samples of methanol in *n*-hexane and in gasoline, which can be clearly discriminated from those for ethanol mixtures. Because of the varieties of ligands with various functional groups,[31–35] the present study provides an effective platform for nanomechanical sensor materials using structure-designed sensitive complexes such as a metal-coordinated complex with structured ligands.

Since the MSS can be portable, the developed sensing system whose detection range of methanol contaminants under ambient conditions covers 1–10% could be practically useful. Not limited by the necessity of ultrahigh sensitive detection for highly toxic substances, 1–10% range selective detection for common chemicals such as methanol is in high demand for daily life activities. For example, methanol-contaminated gasoline and related petroleum products is a world-wide common problem in the automobile and fuel sectors where detection of methanol contaminants with portable devices by easy procedures is required. The current research results will make significant contribution to these social demands.

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Supporting Information

Detailed characterization of Cu(I) complex, detailed sensing performances and supporting tables are summarized in Supporting Information. This material is available on https://doi.org/10.1246/bcsj.20200347.

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Dedicated to Professor Eiichi Nakamura on the occasion of his 70th birthday.

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