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Doctoral Dissertation

Highly Sensitive Gas Detection Using Voids in Organic Salt Crystals and Development of a Sheet Sensor for Practical Application

有機塩結晶中の空孔を利用した高感度ガス検知と
実用化に向けたシートセンサの開発

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December 2023

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General Introduction

Role of gas sensors in industry and environment control

The air we breathe contains a wide variety of chemical species, both natural and man-made, some of which are essential to life, while many others are more or less harmful.^[1] Today, industrial processes increasingly involve the use and production of highly hazardous substances, particularly toxic and flammable gases. Inevitably, occasional gas leaks pose a potential hazard to the industrial plant, its employees and the surrounding community. Therefore, gas sensors, which help to prevent the above problems, play an important role in various modern technological processes where the control and

Table G-1. Some examples of gas sensor applications.^[2a, 8a, 8b]

Field of application	Function	Exmaples of Detected gases
Environment	Monitoring toxic gases present in the atmosphere, due to industrial emissions (weather stations, pollution monitoring)	CO, CH ₄ , humidity, CO ₂ , O ₃ , NO _x , VOCs, SO _x , HCs, NH ₃ , H ₂ S
Safety at work	Control of indoor air quality; monitoring toxic gases in a working environment, for instance in a factory where dangerous chemicals are used	Toxic gases, combustible gases, O ₂
Domestic safety/household application	Detection of poisonous gases or smoke in households, due to accidents such as fires and explosions; intelligent refrigerator or oven; fire alarm; natural gas heating; leak detection; air quality control; air purifiers; cooking control	CO, CH ₄ , humidity, CO ₂ , VOCs
Safety in car	Car ventilation control; gasoline vapor detection; alcohol breath tests	CO, CH ₄ , LPG, VOCs
Public security	Control of indoor air quality, detection of substances dangerous for the safety of the general public	Toxic gases, combustible gases, flammable gases, explosives, O ₂
Medical/clinical	Diagnostics (breath analysis, disease detection); point-of-care patient monitoring; drug monitoring; artificial organs and prostheses; new drug discovery	O ₂ , NH ₃ , NO _x , CO ₂ , H ₂ S, H ₂ , Cl ₂ , anesthesia gases
Agriculture	Plant/animal diagnostics; soil and water testing; meat/poultry inspection; waste/sewage monitoring	NH ₃ , amines, humidity, CO ₂
Food quality control	Detection of particular molecules, which are formed when food starts to rot and it is no longer good for consumption	Humidity, CO ₂ , etc
Utilities/automotive/power plants	Control of the concentration of the gases in the engine and gas boiler, to guarantee the highest possible efficiency of the combustion process. The same concept can also be applied to power plants, as the energy is generated by combustion	O ₂ , CO, HCs, NO _x , SO _x , CO ₂ , H ₂ , HCs
Industry: petrochemical Steel Water treatment Semiconductor	Process monitoring and control; quality control; workplace monitoring; waste stream monitoring; leakage alarms	HCs, conventional pollutants O ₂ , H ₂ , CO, conventional pollutants Cl ₂ , CO ₂ , O ₂ , O ₃ , H ₂ S, CH ₄ H ₂ , CH ₄ , HCl, AsH, BCl ₂ , PH ₃ , CO, HF, O ₃ , H ₂ Cl ₂ Si, TEOS, C ₄ F ₆ , C ₅ F ₈ , GeH ₄ , NH ₃ , NO ₂ , O ₂
Oil and gas		HCs, H ₂ S, CO
Defense/military	Detection of chemical, biological, and toxin warfare agents; treaty verification	Agents, explosives, propellants
Aerospace	Monitoring of oxygen and toxic and flammable gases in the environment atmosphere	H ₂ , O ₂ , CO ₂ , humidity
Traffic/tunnels/car parks	City traffic control and management; air quality monitoring in tunnels or underground parking garages	CO, O ₃ , NO _x , SO ₂ , CH ₄ , LPG

analysis of gases is required.^[2] Gas sensors are now widely used in the following areas: industrial production, such as the detection of methane gas in mines^[3], the automotive sector for the detection of toxic gases from vehicles^[4], medical field applications^[5], indoor air quality monitoring devices^[6], and environmental monitoring, such as the monitoring of greenhouse gases, etc.^[2b, 7]. Table G-1 summarizes the various applications of gas sensors.^[2a, 8]

Gas sensor classification

The basic configuration of the gas sensor is shown in Figure G-1.^[9] The sensing material interacts with the gaseous analytes and subsequently induces a fluctuation in its electrical, dielectric, magnetic, optical, thermometric, acoustic, colorimetric, and/or gravimetric properties, which can be translated into detectable signals by the transducer.

The scientific and industrial communities have worked been working together to create various types of sensors as shown in Table G-2^[10], and in terms of the wide range of application, metal oxide semiconductor sensors and electrochemical sensors dominate the sensor market. On the other hand, in recent years, there has been a growing need in various

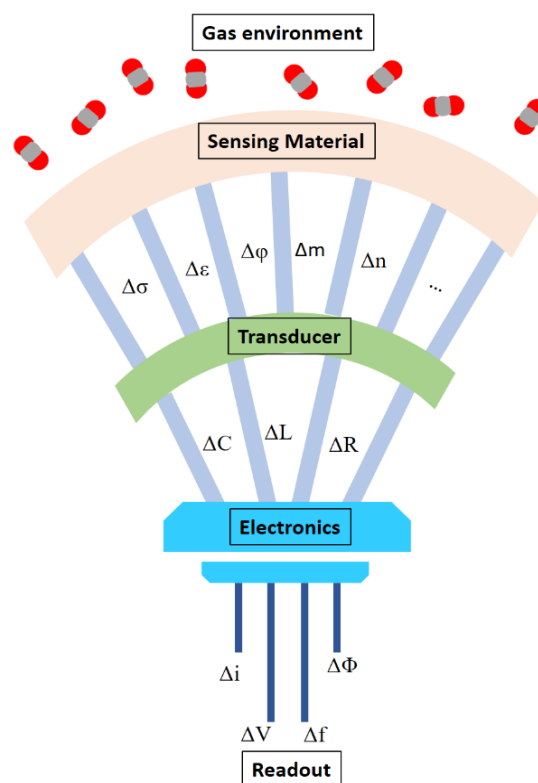


Figure G-1. Basic gas sensor configuration.^[9]

Table G-2. Types of gas sensors.^[10]

Technology	Sensitivity	Selectivity	Suitability of multiple gas detection	Size (dimensions in W × L × H mm)	Power consumption
Metal Oxide semiconductor (MOS)	Sub ppm	Not good	No	2 × 3 × 1	<1 mW
Electrochemical (EC)	100 ppb-ppm	Better than MOS	Only for gases without overlapping	20 × 20 × 4	10-50 μW
Pellistor	1%	Poor	No	14 × 14 × 6	100 mW
Infrared (ND-IR)	Ppm(LED-based) Ppb(Laser-based)	Good	Need to change in the spectrum	26 × 21 × 7	10 mW
Sensor array (e-nose)	Sub ppm	Better than EC and MOS	Yes	Depends on different technology	Depends on different technology

fields for more secure and safer labor-saving and environmentally friendly machine control by digitizing the human senses, and a type of odor sensor called e-nose, which mimics the mechanism of the human nose, is beginning to be put into practical use.

In metal oxide semiconductor sensors, oxygen adsorbed on the metal oxide surface heated by a heater ($>300^{\circ}\text{C}$) reacts with the target gas, causing a change in the sensor resistance, which is measured to estimate the concentration of the target gas (Figure G-2. (a)).^[11] The metal oxide portion on which the gas is adsorbed consists of n-type metal oxides such as tin oxide and zinc oxide, which can be fabricated using a semiconductor process, allowing metal oxide semiconductor sensors to be mass-produced at a relatively low cost. In principle, they have the disadvantage of poor gas selectivity.^[12] Another problem is their high power consumption due to operation at high temperatures of several hundred degrees Celsius.

Electrochemical gas sensors use a redox reaction to obtain gas concentration.^[13] The gas molecules to be detected undergo an oxidation reaction at the sensing electrode, producing ions and electrons. The ions are transferred to the counter electrode via the electrolyte, and the electrons are transferred to the counter electrode via an external circuit, causing a reduction reaction. Since the current flowing through the external circuit increases in proportion to the gas concentration, the gas concentration can be calculated by monitoring the current value (Figure G-2. (b)). On the other hand, they are sensitive to temperature and humidity, and require regular maintenance due to their unstable response and short life.^[10, 14]

The e-nose type sensor has an array structure with multiple transducers equipped with sensitive membranes having different affinities, and is characterized by capturing the odor not as a quantitative analysis but as a pattern that gives a bird's eye view of the portfolio of chemical substances composing odor (Figure G-2. (c)).^[15] The membrane-type surface-stress sensor (MSS) developed by Yoshikawa et al. detects the surface stress induced by the adsorption and desorption of target gas molecules on the receptor layer coated on a silicon membrane with extremely high sensitivity.^[16] MSS can be fabricated by semiconductor processes, and their application as e-nose, in which multiple MSS with different sensor films are arranged to identify the gas species from their response patterns, is currently in progress.^[16f, 17] Suslick et al. reported an e-nose type sensor in which multiple dyes such as polyphilin and pH indicator are arranged in an array and the gas species is identified from the color change pattern of the dyes upon exposure to the target gas.^[18] These e-noses are strongly expected to be a tool that can be used for quality control of raw and manufactured products, process design, freshness and

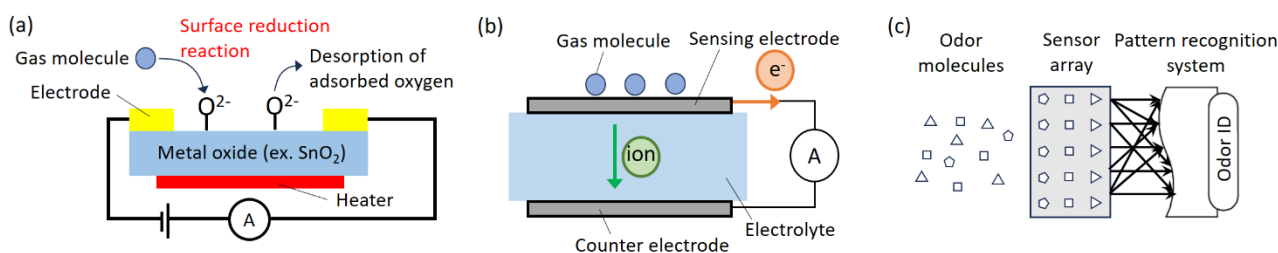


Figure G-2. Schematic diagrams of (a) metal oxide semiconductor gas sensor, (b) electrochemical gas sensor, and (c) e-nose type gas sensor.

ripeness monitoring, shelf life investigation, authenticity assessment of premium products, classification of scents and perfumes, and early diagnosis of diseases.^[19] However, the practical application of e-nose presents a great number of challenges, such as accumulating training data for pattern recognition, ensuring reproducibility of individual sensor responses, and preventing interference from water vapor in the air.

Requirements of gas sensors

The main purpose of any gas sensor is to provide reliable real-time information about the chemical composition of the surrounding environment. Ideally, therefore, a gas sensing device should operate continuously and reversibly, without disturbing the sample. An ideal gas sensor should be low cost and foolproof, operating with perfect and instantaneous selectivity with respect to a specific target gas, which is present in the surrounding environment. The device should produce a measurable signal output at any desired gas concentration.^[20] Ease of fabrication, fast response, achievement of minimal measurement uncertainty, insensitivity to relative temperature and humidity, high resistance to contamination and poisoning, and low noise are also useful requirements of the gas sensor designed for the gas sensor market. The ideal sensor should be portable and enclosed in a small, explosion-proof housing, making it suitable for use in hazardous locations and harsh environments.^[21] For portable applications, the ideal gas sensor should be small and have low power consumption. In addition, it should require minimal special training for personnel to operate and maintain the sensor. Gas sensors should provide repeated measurements of analytes over time in multiple or remote locations to support environmental monitoring. The ideal sensor should operate continuously and reliably for at least 30 days without the need for recalibration. Such a gas sensor should be able to function in an industrial environment for at least 2 years or longer, and should be replaceable or renewable at a reasonable cost. The required level of quantitative reliability, such as precision and accuracy, should also be provided.

However, it is important to note that, despite the great advances made over the last few decades, there is no such ideal gas sensor on the market today.^[2d] There is currently no gas sensor that meets all of these requirements, and there is always some drawback. Therefore, when designing gas sensors, the first step is to try to meet the requirements of the intended application. For example, high reliability, adequate long-term stability, a low false-positive rate, and good sensitivity are high on the priority list of industrial sensor users, while size and the cost of sensors are often the least important factors. In contrast, medical users focus on the cost of disposable sensors.^[22] Since gas sensors intended for environmental monitoring do not, in principle, require extremely high sensitivity, gas sensors with different sensitivity, selectivity, and other characteristics can be used. In other words, when designing a new gas sensor, we must first clarify the minimum requirements that are essential for the actual form of use in the intended application. And then, to meet these requirements, the specifications for each

component, such as sensing materials and transducers, as well as for the entire sensor system, should be determined. The requirements for sensing materials are discussed below.

Materials Acceptable for Gas Sensor Applications

The results of much research have shown that, in theory, any material can be used in the design of gas sensors, regardless of its physical, chemical, structural, or electrical properties. Prototypes of gas sensors based on covalent semiconductors, semiconducting metal oxides, solid electrolytes, polymers, ionic membranes, organic semiconductors, and ionic salts have already been tested. As shown in Table G-3, these materials can be successfully used in the design of all types of gas sensors, including humidity sensors. It has been established that various materials can show excellent adaptability for application in gas sensors.^[23] However, despite the large number of materials used for gas sensors, only a few materials have been used in the actual sensor market. The majority of the devices available in the sensor market are elaborately manufactured using only on sensing materials such as metal oxides and polymers, which can be referred to as traditional or conventional sensing materials.

Table G-3. Typical materials used in gas sensor research and development.^[2d, 23]

Material	Examples	Analyte (function in sensors)
Metals	Pt, Pd, Ni, Ag, Au, Sb, Rh	Gases (H ₂ , etc.) (electrodes, sensing materials, catyalysts, membranes)
Semiconductors	Si, GaAs, InP, SiC, GaN, etc	Gases (O ₂ , CO ₂ , H ₂ S, CH ₄ , NO ₂ , OC. Etc.); H ₂ O. etc (sensing materials)
Metal Oxides	Electronic conductors (SnO ₂ , TiO ₂ , In ₂ O ₃ , etc.); mixed conductors (Ga ₂ O ₃ , WO ₃ , SrTiO ₃ , perovskites); ionic conductors (ZrO ₂ , CeO ₂ , etc.); metal oxides with metallic-type conductivity (RuO ₂ , Co ₃ O ₄ , PbO _x , etc.)	Gases(CO, H ₂ , CH ₄ , NO _x , O ₂ , Cl ₂ , etc. vapor, alcohol; dissolved oxygen O ₂ , Cl ₂ in solutions; dissolved oxygen in molten metals, etc. (electrodes, sensing materials, membranes)
Ionic compounds	Ionic conductors [LaF ₃ , CaF ₂ , Na ₂ CO ₃ , AgCl, Zr(HPO ₄) ₂ , SrCl ₂ , Na ₂ SO ₄ , AgBr, Ag ₂ S, CuBr, Nasicon, Nafion]	Gases (CO ₂ , SO ₂ , CO, etc.), ions, etc. (sensing materials, electrodes, membranes)
Molecular crystals	Phthalocyanines [PbPc, LuPc ₂ , LiPc, FePc, CuPc, NiPc, (PcAlF) _n , etc.]	Gases, vapors, ions (sensing materials, membranes)
Langmuir-Blgett films	Phthalocyanines, polydiacetylenes, Cd-arachidate, etc	Gases (NO ₂ , NH ₃ , Cl ₂ , etc.), vapors, etc. (sensing materials, membranes)
Membranes	Ion-exchange membranes; neutral-carrier membranes; charge carrier membrane	Cations, anions in solutions; gas filtration (membranes)
Cage compounds	Zeolites, calixarenes, cyclodextrines, crown ethers, cyclophanes, etc.	Gases, vapors (membranes, supporting media)
Carbon	Carbon nanotubes, black carbon, diamond, fullerenes, graphene	Gases, vapors (sensing materials, electrodes, membranes)
Polymers, Organic semiconductors	Polyethers, polyurethanes, polysiloxanes, polypyrroles, polythiophenes, polyolefins, polyphnyl acetylene, phthalocyanine, polyamides, polyimides, polyfluorocarbons, polyetrafluoroethylene, Nafion, etc	Gases (CO, CO ₂ , CH ₄ , NO _x , etc.), H ₂ O, chlorinated, hydrocarbones, etc. (sensing materials, membranes)

Materials targeting the sensor market should meet a variety of stringent requirement such as: (1) strong response to the target gas, (2) low cross sensitivity, (3) wide measurement range, (4) long operating /

field life, (5) fast and reversible interaction with analytes, (6) low sensitivity of the signal to a change in air humidity, (7) absence of long term drift, (8) short time to operational state, (9) effective low cost technology, (10) high reproducibility, and (11) uniform and strong binding to the surface of the substrate. Many different materials appear to be advantageous with respect to some of these properties, but very few materials are promising with respect to all of these requirements.^[24] Since the priority of these requirements varies depending on the purpose and application, it is necessary to take the approach of excluding low priority requirements. For example, (4) and (5) can be excluded for disposable applications, and (3) is unnecessary for applications where the concentration range of measurement can be limited to a narrow range. By targeting the requirements to be prioritized according to purpose and application, it is possible to concentrate on improving the essential material functions.

Many applications require gas sensors with high selectivity and the choice of sensing material should therefore take this requirement into account. Over the years, various approaches have been explored to develop materials with molecular selectivity, including the use of molecularly imprinted polymers, zeolites, metal organic frameworks (MOFs), covalent organic frameworks (COFs) and other supramolecular compounds. In particular, MOFs, which are constructed via coordination bonds between organic linkers and metal ions, are more desirable than conventional polymers, zeolites, and other inorganic materials in terms of topology, pore size and geometry, and even tailored response to external stimuli by different metal ion and organic ligand selections (Figure G-3).^[25] The development of MOF-based gas sensors over the last two decades has been largely driven by the advances in the design and synthesis of MOFs and the study of their physicochemical properties.

The MOF-based gas sensors have the following advantages.^[26] First, MOFs are permanently porous, providing a large specific surface area and potential active sites for gas uptake and transport. This feature allows for the preconcentration of the target gas, thereby improving the sensitivity. Second, the tailored pore size/shape and physicochemical environment of MOFs allows selective adsorption for specific analytes, increasing selectivity and sensitivity. Third, structural identification and property

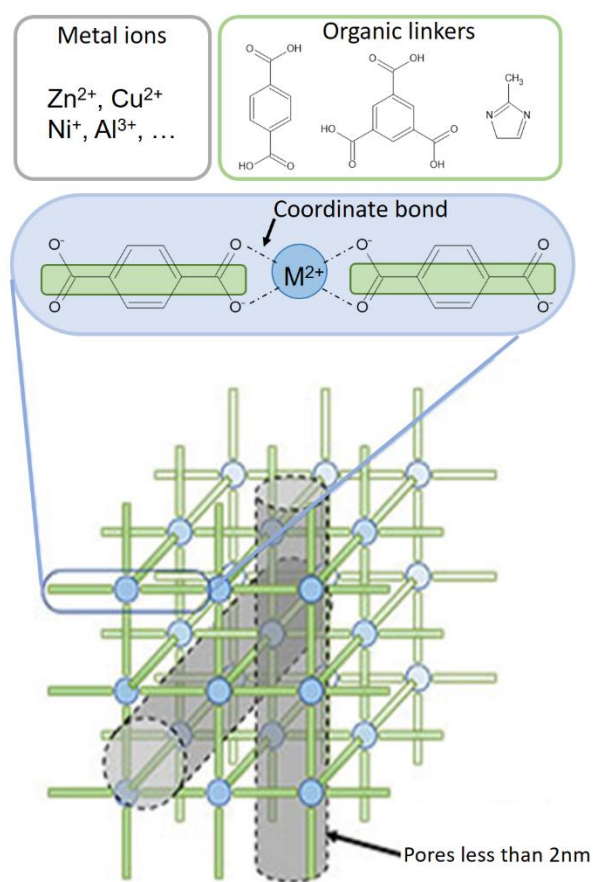


Figure G-3. Schematic diagram of the skeletal structure of MOF.

correlation related to host-guest interactions at the molecular/atomic level is possible due to the relatively good crystallinity and predictable periodic arrangement of atoms/molecules in MOFs.

The operating principles of MOF-based gas sensors are primarily based on molecular recognition and the subsequent conversion of the recognition events into detectable signals.^[27] The former involves the interaction between the target gas and the MOFs, which are characterized by large specific surface areas, controllable pore sizes/geometries, and host-guest interactions. Unlike disordered networks such as polymers, MOFs with precisely tuned pore environments offer unique advantages in selective molecular recognition due to the well-known molecular sieve effect. The latter refers to the fluctuations in electrical, dielectric, magnetic, optical, thermometric, acoustic, colorimetric, and gravimetric properties induced by the above interactions, which can be interpreted into signals measurable by the transducer. In particular, the interactions are typically non-covalent interactions such as van der Waals forces, hydrogen bonding, and π - π interactions, which allow reversible uptake and release toward the analyte, leading to reversible sensing events.^[26] However, possible covalent bonding or redox reactions between the target gas and selected reactive MOFs can cause irreversible responses with higher selectivity and sensitivity.^[28]

In order to expand the application of MOF-based gas sensors as a practical advanced technology, the formation of large-area MOF films on solid substrates is the key. A variety of methods have been reported so far for the preparation of MOF films on various surfaces, including direct hydro/solvothermal growth, direct deposition assisted by spin/dip coating,^[29] layer-by-layer or stepwise growth,^[30] electrochemical deposition,^[31] interfacial synthesis approach coupled with a subsequent transfer,^[32] and template-mediated growth/transformation.^[33] However, it remains difficult to form large-area (typically at least several cm²) MOF films with good homogeneity. This is because the formation of most MOFs is based on the hydro/solvothermal approach, and the area of MOF films obtained by the direct growth/deposition method is largely limited by the volume of the containers typically used. In addition, most MOF powders have poor processability, which limits the fabrication of large area MOF films.^[34] Therefore, it is desirable to develop porous crystalline materials with better processability than MOFs.

While MOFs are metal complex-like structures utilizing coordination bonds between organic linkers and metal ions, porous molecular crystals utilizing non-covalent interactions such as hydrogen bonding have also been extensively studied in recent years.^[35] Hisaki et al. succeeded in constructing a robust hydrogen-bonded organic frameworks (HOFs) by incorporating a versatile and bond-directed carboxy group into a rigid π -conjugated system and allowing multiple hydrogen bonds and π / π interactions to act cooperatively.^[36] For example, the quinoxaline-annelated [12]annulene derivative (TQ12) with six peripheral carboxyphenyl groups was used to construct HOF, which exhibited a reversible response to HCl with a color change.^[36f]

Our group promotes research focusing on organic salts constructed by strong ionic hydrogen bonding (charge-assisted hydrogen bonding) that act between acidic carboxy or sulfonic groups and basic amino groups. The combination of an organic acid acting as a functional moiety and an amine acting as a structural control moiety allows the construction of different higher order crystal structures and the addition of different functions and physicochemical properties.^[37] In particular, when triphenylmethylamine (TPMA) is used as an amine molecule, the sulfonic acid and TPMA form [4+4] tetrahedral supramolecular clusters through charge-assisted hydrogen bonding, and these clusters accumulate hierarchically to form porous organic salts (POSs).^[38] It was reported that POS composed of stilbene-4,4'-disulfonic acid (SBDS) and TPMA exhibited reversible fluorescence switching in response to specific volatile organic compound (VOC) gas molecules.^[38c]

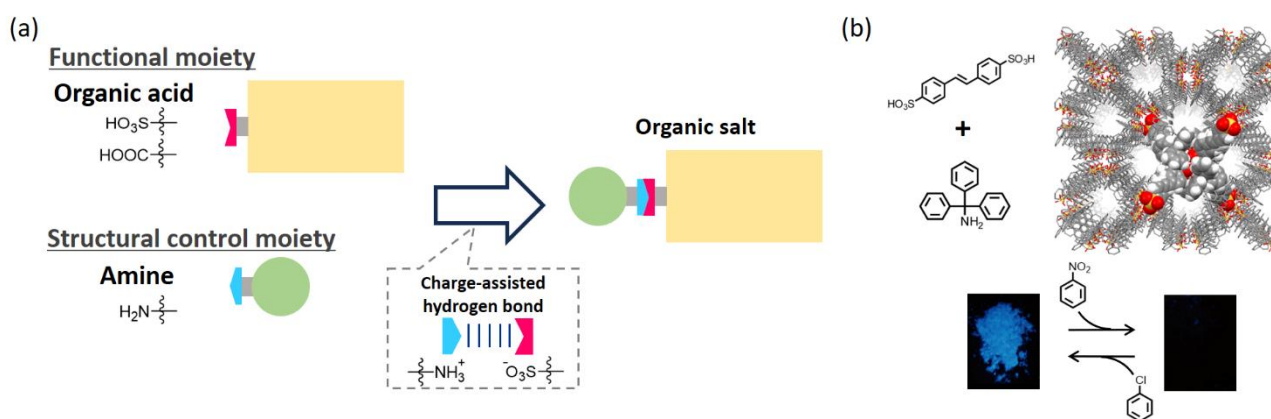


Figure G-4. (a) Formation of an organic salt by charge-assisted hydrogen bonding. (b) The POS composed of SBDS and TPMA with reversible switching of fluorescence in response to specific VOC guest molecules. ^[38c]

Unlike the neutral hydrogen bonds that form HOFs, the charge-assisted hydrogen bonds that form organic salts are very strong and therefore structurally robust. In addition, the hydrogen bonding is reversible, so not only can the structures be easily constructed by simply recrystallising them from solution, but the same structures can also be reconstructed by redissolving them. This means that they have the remarkable property of good solubility in certain solvents, and it is possible to arrange porous crystals over a large area on a solid substrate by a very simple solution process. Therefore, organic salts have the potential to become industrially viable sensing materials as an alternative to MOFs.

Scope of this thesis

Based on the above background, this thesis describes practical gas sensing materials using organic salt crystals with excellent processability. By appropriately designing the combination of organic acid molecules, which interact with the target gas to change its fluorescence, and amine molecules, which control the molecular arrangement in the crystal to specifically scavenge the target gas, the author can construct organic salt crystals with void structures that can selectively detect the target gas with high sensitivity. Furthermore, the concept of a process for the fabrication of large-area sensor sheets, which takes advantage of the high processability of organic salts, is shown in Figure G-5. When the redissolved solution of organic salts is contained in the macropores of a porous support such as a membrane filter or filter paper and then dried, microcrystals of organic salts are precipitated in the pores, and a large-area organic salt-immobilized sensor sheet with high in-plane uniformity can be fabricated in an extremely simple manner.

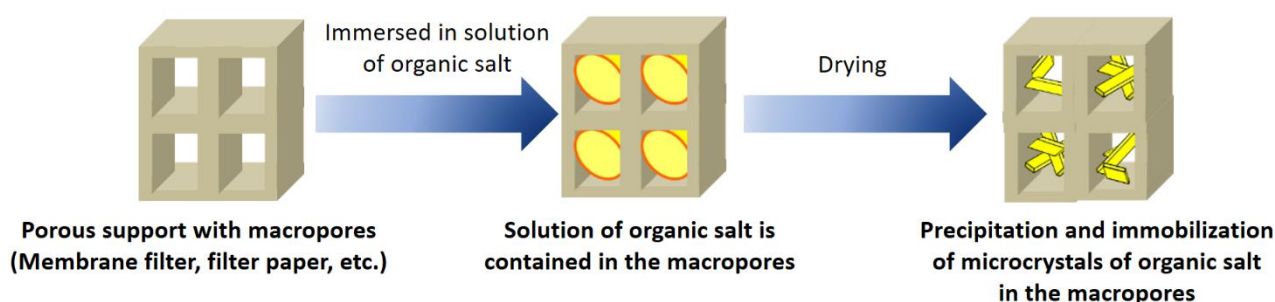


Figure G-5. Schematic representation of immobilization of organic salts on a porous support with macropores.

Chapter 1 describes a novel material capable of detecting gaseous OH radical ($\cdot\text{OH}$). The author found that organic salts consisting of terephthalic acid and *n*-alkylamine (alkyl chain length is >8) selectively scavenge gaseous $\cdot\text{OH}$ and exhibit a fluorescence emission response. It was also demonstrated that the organic salt crystals could be immobilized on a porous membrane filter by a simple solution process to produce an $\cdot\text{OH}$ detection sheet.

Chapter 2 describes guidelines to further improve the $\cdot\text{OH}$ detection performance for the practical application of the $\cdot\text{OH}$ detection method using the *n*-alkylammonium terephthalate immobilized sheets discussed in Chapter 1. The effects of the alkyl chain length of the *n*-alkylamines and the pore size of the membrane filters on the fluorescence response performance were investigated in detail. A method for quantitative visualization of the spatial distribution of gaseous $\cdot\text{OH}$ was also demonstrated.

Chapter 3 describes a POS, consisting of 2-cyano-3(4-((4-methoxyphenyl)(phenyl)amino)phenyl)acrylic acid and TPMA, which can selectively detect ammonia at sub-ppm levels. It was demonstrated that the POS could be immobilized on a porous support, a filter paper, by the same simple solution process described in Chapters 1 and 2, resulting in an ammonia detection sheet.

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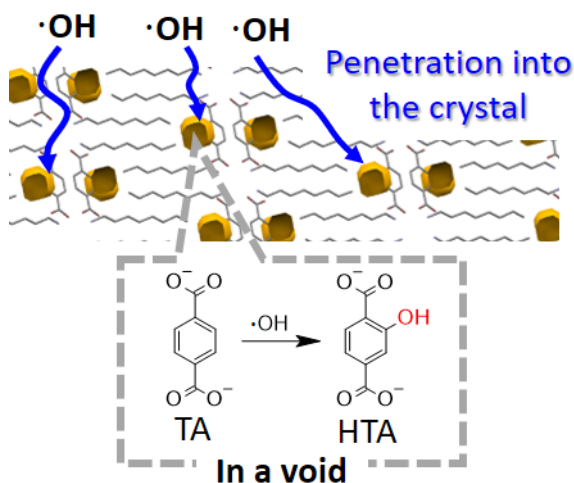
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Chapter 1

Primary Ammonium Terephthalate Salts with High Moisture Resistance and Their Use in the Detection of OH Radical



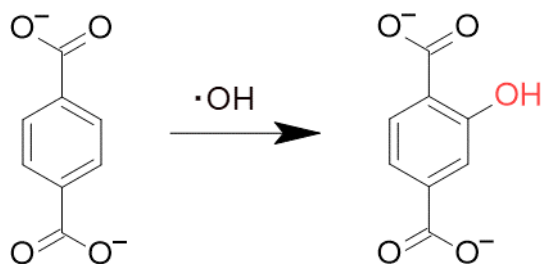
Abstract: This chapter describes a novel and practical method for the detection of gaseous OH radical ($\cdot\text{OH}$) using a moisture-resistant organic salt composed of terephthalic acid (TPA) and *n*-alkylamine. When the alkyl chain length was greater than 8, the organic salt had a crystal structure in which the alkyl chains were arranged parallel to each other and zero-dimensional voids were adjacent to terephthalate (TA). Since the parallelly arranged alkyl chains acted as a hydrophobic block, the organic salts had excellent moisture resistance. The highly hydrophobic bis(*n*-octylammonium) terephthalate (nOA-TA) powder was exposed to gaseous $\cdot\text{OH}$ generated by a low-pressure mercury lamp and a fluorescence response suggesting the formation of hydroxyterephthalate (HTA) was observed. The presence of the zero-dimensional voids in the nOA-TA crystal caused the formation of HTA. In addition, a sheet was prepared on which nOA-TA crystals were uniformly immobilized in the pores of a membrane filter, and the spatial distribution of $\cdot\text{OH}$ was evaluated.

1.1 Introduction

The active oxygen OH radical ($\cdot\text{OH}$) is generated by UV lamps and plasma processes, has very strong oxidizing power, and is widely used in various surface treatment applications, e. g., surface cleaning,^[1] modification,^[2] and sterilization.^[3] Although these $\cdot\text{OH}$ are important in various processes, their lifetime is short, from microseconds to milliseconds,^[4] and it is not easy to measure their spatial concentration distribution on-site.

As a method for directly measuring $\cdot\text{OH}$ in a given space, a laser-induced fluorescence (LIF) method is known, in which a laser beam is irradiated to measure fluorescence emissions accompanying electronic excitation and de-excitation of $\cdot\text{OH}$.^[5]

In electron spin resonance spectroscopy (ESR), a stable organic radical is formed by reacting an $\cdot\text{OH}$ with spin trapping agents such as 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), and the $\cdot\text{OH}$ is indirectly measured by measuring its ESR spectrum.^[6]



Scheme 1-1. Formation of hydroxyterephthalate (HTA) via the reaction of terephthalate (TA) with OH radical.

Terephthalate (TA) is used as a dosimetry of $\cdot\text{OH}$ since it does not react with other active oxygens, such as superoxide anion radical, hydroperoxyl radical, and hydrogen peroxide. The $\cdot\text{OH}$ is indirectly measured from the fluorescence around 420 nm of hydroxyterephthalate (HTA) formed by the reaction of the $\cdot\text{OH}$ with terephthalate (Scheme 1-1).^[7]

LIF requires large and expensive lasers and photodetectors, and is not suitable for on-site measurements. Reactions of spin trapping agents and terephthalate with $\cdot\text{OH}$ have been reported only when they are in aqueous solutions, greatly limiting embodiments of on-site measurements of $\cdot\text{OH}$.

In order to measure the spatial distribution of $\cdot\text{OH}$, a material that scavenges $\cdot\text{OH}$ in the solid state is indispensable. To the best of our knowledge, however, such materials have not been reported.

For application to measurements over a wide range of humid atmospheres, solid scavengers must have excellent moisture resistance. On the other hand, if such scavengers can be dissolved in any solvent other than water, it becomes easy to uniformly immobilize them over a wide range on a support such as a porous sheet, which is desirable for measuring the spatial distribution of $\cdot\text{OH}$. Thus, a solid $\cdot\text{OH}$ scavenger must be insoluble in water but soluble in some solvent other than water. Therefore, spin trapping agents such as DMPO are unsuitable because they are easily dissolved in water. Terephthalate

salts with cations such as Na^+ , K^+ , and NH_4^+ are also soluble in water.^[8] On the other hand, terephthalic acid (TPA), which is not a salt, is poorly soluble in water and alcohols, but soluble in dimethyl sulfoxide (DMSO).^[9] The crystal structure of TPA is closely packed by the π - π interactions between the benzene rings,^[10] preventing $\cdot\text{OH}$ from penetrating into the crystal. Thus, the reaction between $\cdot\text{OH}$ and terephthalic acid occurs only on the crystal surface, which leads to low production efficiency of HTA.

Yuge *et al.* described primary ammonium terephthalate salts that formed supramolecular synthons through various charge-assisted hydrogen bonded networks.^[11] These organic salts are soluble in organic solvents such as methanol and ethanol. It is expected that highly hydrophobic organic salts can be developed by appropriately selecting the substituents of the primary ammonium cation. In addition, since the substituents function as spacers, a “gap” in which $\cdot\text{OH}$ can penetrate into the inside of the crystal is formed. Thus, there is a possibility that the specific surface area in which $\cdot\text{OH}$ react with terephthalate increases and the production efficiency of HTA is improved.

In this report, *n*-alkyl groups were selected as the substituents of the primary ammonium cation. Alkyl groups have various properties such as flexibility, cohesiveness, and solubilization, and are highly versatile substituents that can be introduced into various compounds according to their intended purpose. For example, in self-assembled monolayers (SAMs) such as *n*-alkanoic acid and *n*-alkyl phosphate, the microscopic molecular arrangement depends on the alkyl chain length. As the chain lengthens, the cohesive interaction between molecules increases and the chain is pulled in to form well-ordered and densely packed monolayers.^[12]

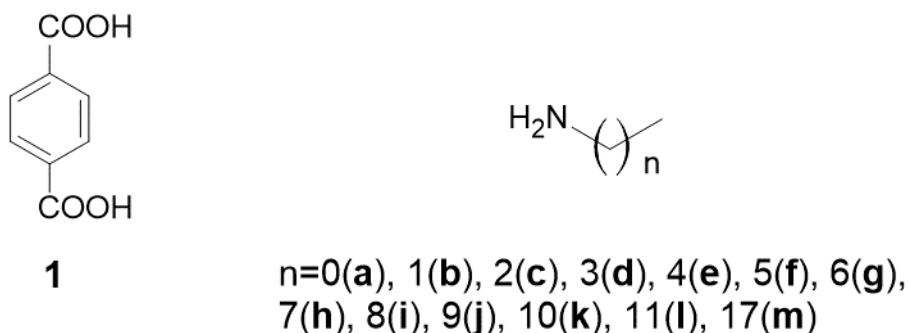
Yuge *et al.* reported the crystal structure of bis (*n*-butylammonium) terephthalate in which the *n*-butyl group was bent at the α -position.^[11b] By introducing long chain alkyl groups, it may be possible to achieve molecular arrangements similar to SAMs^[12a, 12b] in organic salt crystals.

Herein, the author prepared *n*-alkylammonium terephthalate salts with various alkyl chain lengths and investigated the relationship between their moisture resistance and crystal structures. The highly hydrophobic bis (*n*-octylammonium) terephthalate (nOA-TA) crystal powder was exposed to gaseous $\cdot\text{OH}$ generated by the low-pressure mercury (Hg) lamp method, and their fluorescence responsivity was evaluated and compared with TPA. In addition, the author prepared a sheet in which nOA-TA crystals were uniformly immobilized in the pores of a membrane filter, and evaluated the spatial distribution of $\cdot\text{OH}$.

1.2 Experimental section

1.2.1 Preparation of organic salts composed of TPA and *n*-alkylamines

All chemicals and solvents were commercially available and used without any purification. The *n*-alkylamines with various chain lengths used here are described in Scheme 1-2. They were mixed with TPA at a 2 : 1 molar ratio in methanol and evaporated to yield crystal powders of organic salts.



Scheme 1-2. Terephthalic acid (**1**) and *n*-alkylamines (a–m).

1.2.2 Preparation of single crystals

Crystal powders of **1f**, **1g**, **1h**, **1i**, **1k**, and **1l** were dissolved in a mixture of methanol/acetonitrile. Slow evaporation of the solvent at room temperature gave single crystals.

1.2.3 Crystallographic analysis of single crystals

The X-ray diffraction data of the single crystals of **1f**, **1g**, **1h**, **1i**, **1k**, and **1l** were collected on a two-dimensional X-ray detector (PILATUS 200 K/R) equipped with a Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu–K α radiation ($\lambda=1.54187$ Å) at 213 K. The cell refinements were performed with CrysAlisPro 1.171.39.5a software.^[13] The crystal structure was solved by direct method (SHELXT Version 2014/5).^[14] All calculations were performed with the observed reflections [$I > 2\sigma(I)$] with the CrystalStructure crystallographic software package,^[15] except for refinement which was performed by SHELXL.^[16] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. Deposition Numbers 2026833 (for **1f**), 2026834 (for **1g**), 2026835 (for **1h**), 2026836 (for **1i**), 2026839 (for **1k**), and 2026840 (for **1l**) contain the supplementary crystallographic data for this chapter.

1.2.4 Fluorescence spectroscopy measurements

Fluorescence spectra were measured with 310 nm excitation light from an LED source (Ocean Optics, LLS-310) and the spectrometer (Andor Technology, Shamrock SR-303i). A detailed measurement system is shown in Figure 1-1.

1.2.5 Preparation of Bis (*n*-octylammonium) hydroxyterephthalate (nOA-HTA)

2-Hydroxyterephthalic acid and *n*-octylamine (**h**) were mixed in methanol in a 1 : 2 molar ratio. The solution was evaporated to yield a white crystal powder of the salt.

1.2.6 Powder X-ray diffraction analysis

Powder X-ray diffraction (PXRD) patterns were measured by using a Rigaku Ultima IV with graphite-monochromatized Cu K α radiation ($\lambda=1.54187$ Å) at room temperature.

1.2.7 Scanning electron microscopy (SEM) measurements

SEM images were taken with a Hitachi High Tech SU8220 in the SE+BSE (TU) mode.

1.2.8 Fluorescence image acquisition

Fluorescence images were taken with irradiation of 313 nm light from a 250 W mercury light source (Asahi Spectra, REX-250). A detailed measurement system is shown in Figure 1-2.

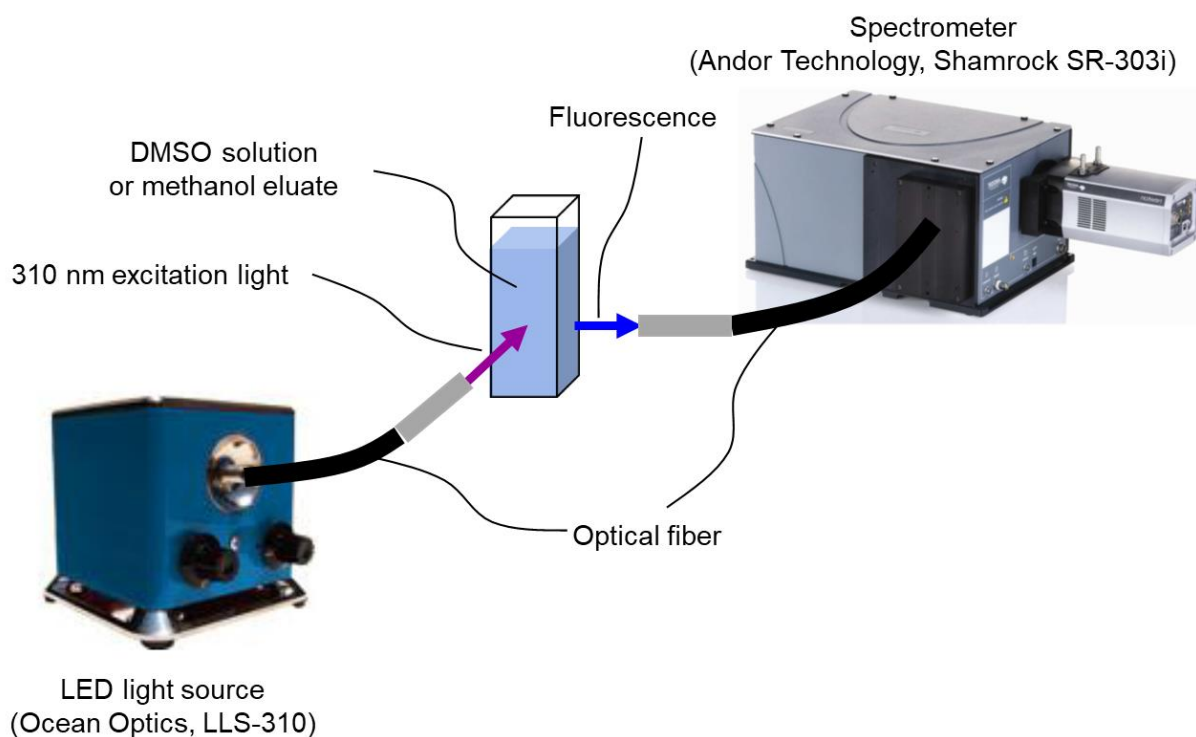


Figure 1-1. Schematic diagram of an experimental system for fluorescence spectroscopy measurements.

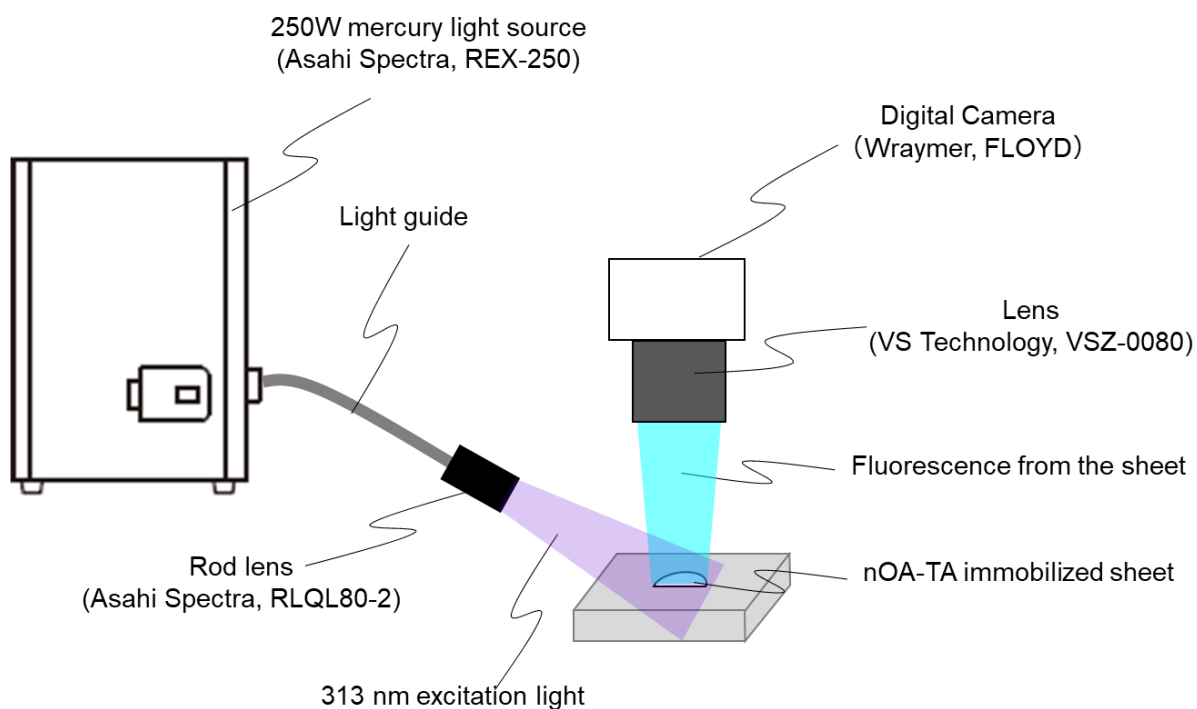


Figure 1-2. Schematic diagram of an experimental system for fluorescence image acquisition.

1.3 Results and Discussion

1.3.1 Crystal structures and water vapor resistance of *n*-alkylammonium terephthalate salts

Approximately 4 mg of each of the organic salt crystal powders were placed in an aluminum pan and exposed to humidified air above 95 %RH (RH: Relative Humidity) for 24 hours. Figure 1-3 shows photographs of powders taken before and after exposure to humidified air. Powders containing 7 or less carbon atoms in the *n*-alkyl group (**1a–1g**) and disodium terephthalate (Na-TA) were partially or completely deliquescent after exposure to humidified air. On the other hand, when the *n*-alkyl chain length was 8 or more (**1h–1m**), humidified air had no effect on the morphology of the powders.

Molecular arrangements of **1f**, **1g**, **1h**, **1i**, **1k**, and **1l** in the powder crystal state were revealed by X-ray single-crystal analysis. The crystals of the hydrophobic organic salts (**1h**, **1i**, **1k**, and **1l**) had structures in which the alkyl chains were pulled in with all-*trans* zigzag conformations and aligned parallel to each other. More interestingly, zero-dimensional voids existed in the vicinity of terephthalate (Figure 1-4c, 4d, 4e, and 4f). In contrast, in the crystal of the deliquescent organic salts (**1f** and **1g**), the alkyl chains were not aligned in parallel and no voids were observed (Figure 1-4a and 4b).

At alkyl chain lengths greater than 8, it is likely that cohesive interactions between the alkyl groups acted to allow them to assemble more closely, resulting in a parallel integrated structure similar to

SAMs.^[12a, 12b] It is considered that the accumulated structure of the alkyl chains act as a hydrophobic block and exhibits high water vapor resistance.

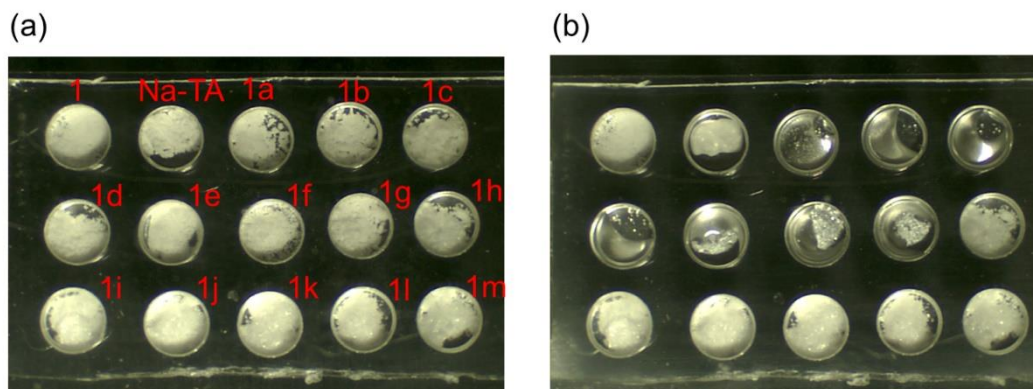


Figure 1-3. (a) Photograph of powders before exposure to humidified air. (b) Photograph of powders after exposure to humidified air above 95 %RH.

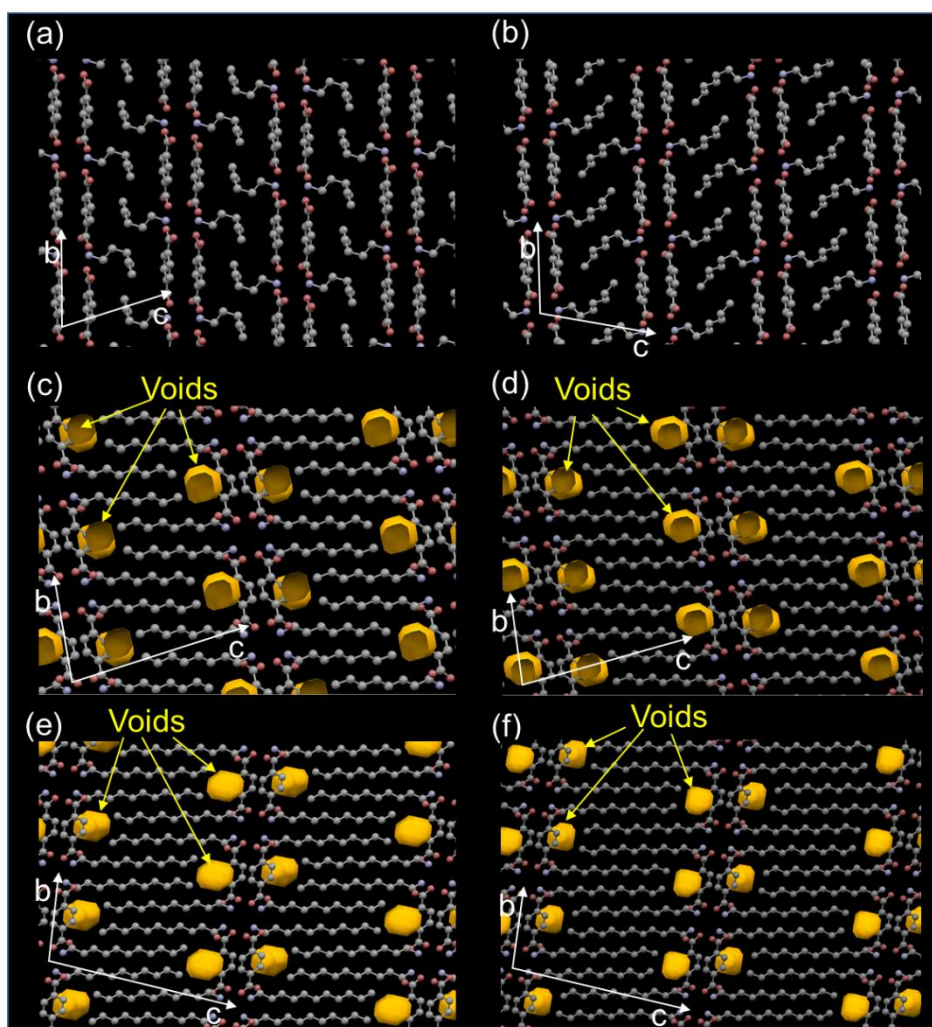


Figure 1-4. Crystal structures of (a) 1f, (b) 1g, (c) 1h, (d) 1i, (e) 1k, and (f) 1l. The yellow-colored void spaces are visualized by mercury with a probe radius of 1.2 Å and a grid spacing of 0.7 Å.

Table 1-1. Crystallographic parameters of **1f**, **1g**, **1h**, **1i**, **1k**, and **1l**.

Crystal	1f	1g	1h	1i	1k	1l
Formula	C ₁₄ H ₂₀ NO ₄	C ₁₅ H ₂₃ NO ₄	C ₂₄ H ₄₄ N ₂ O ₄	C ₂₆ H ₄₈ N ₂ O ₄	C ₃₀ H ₅₆ N ₂ O ₄	C ₃₂ H ₆₀ N ₂ O ₄
<i>F</i> _w	266.32	281.35	424.62	452.68	508.78	536.84
Crystal System	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space Group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)
<i>a</i> [Å]	6.73319(12)	6.71351(13)	7.70797(16)	7.6052(2)	7.5513(2)	7.57798(12)
<i>b</i> [Å]	9.7676(2)	9.7486(2)	10.3459(3)	10.1977(3)	10.2147(2)	10.37400(15)
<i>c</i> [Å]	11.7976(2)	12.5263(5)	17.3715(5)	19.1021(6)	21.6254(5)	22.5340(4)
α [°]	71.319(2)	99.215(2)	82.100(2)	81.878(3)	96.8656(17)	94.7077(14)
β [°]	73.5798(18)	101.561(2)	88.988(2)	89.128(3)	90.329(2)	91.6183(14)
γ [°]	80.0368(17)	99.4258(19)	78.826(2)	80.609(3)	99.258(2)	101.0190(13)
<i>V</i> [Å ³]	702.13(2)	776.38(4)	1346.09(6)	1446.91(7)	1633.99(7)	1731.21(5)
<i>Z</i>	2	2	2	2	2	2
<i>d</i> _{calcd} [g m ⁻³]	1.260	1.203	1.048	1.039	1.034	1.030
<i>R</i> ₁ [I>2σ(I)]	0.0626	0.093	0.0459	0.0767	0.0835	0.0466
<i>wR</i> ₂ (all data)	0.1854	0.3196	0.1458	0.2468	0.2853	0.1519
2θ _{max} [°]	148.2	148.2	148.8	148.4	148.9	149.1
CCDC No.	2026833	2026834	2026835	2026836	2026839	2026840

1.3.2 Fluorescence responsivity to ·OH produced by low-pressure Hg lamp method

An acrylic box with a sapphire window, a goniometric stage, and a low-pressure Hg lamp (KYOKKO, GL-4Z) were arranged as shown in Figure 1-5a. The surface of the goniometric stage was tilted about 28 degrees. The height of the goniometric stage was adjusted so that the height of the side at the highest position along the surface coincided with the height of the upper side of the sapphire window.

The aluminum sample pans were filled with 6.6×10^{-5} mol of TPA and 4.7×10^{-6} mol of **1h** (nOA-TA) crystal powder and then pressed with a press machine to produce pellets. Two pellets were aligned along the highest side on the inclined surface of the goniometric stage.

The inside of the acrylic box was depressurized to remove oxygen to a concentration of about 0.2 %, and humidified nitrogen was passed through to adjust the relative humidity to 95 %RH. In this condition, the low-pressure Hg lamp was irradiated through the sapphire window of the acrylic box for 2 hours. During this time, water molecules in the humidified nitrogen atmosphere were decomposed by vacuum ultraviolet (VUV) light of 185 nm from the low-pressure Hg lamp, and gaseous ·OH was generated^[17] and exposed to the pellets. The pellets were placed near the top of the sapphire window with the goniometric stage on which the pellets were placed tilted 28 degrees to avoid direct exposure to the light from the low-pressure Hg lamp. Oxygen was removed by decompression in order to suppress the generation of active species other than ·OH, such as ozone, by subsequent

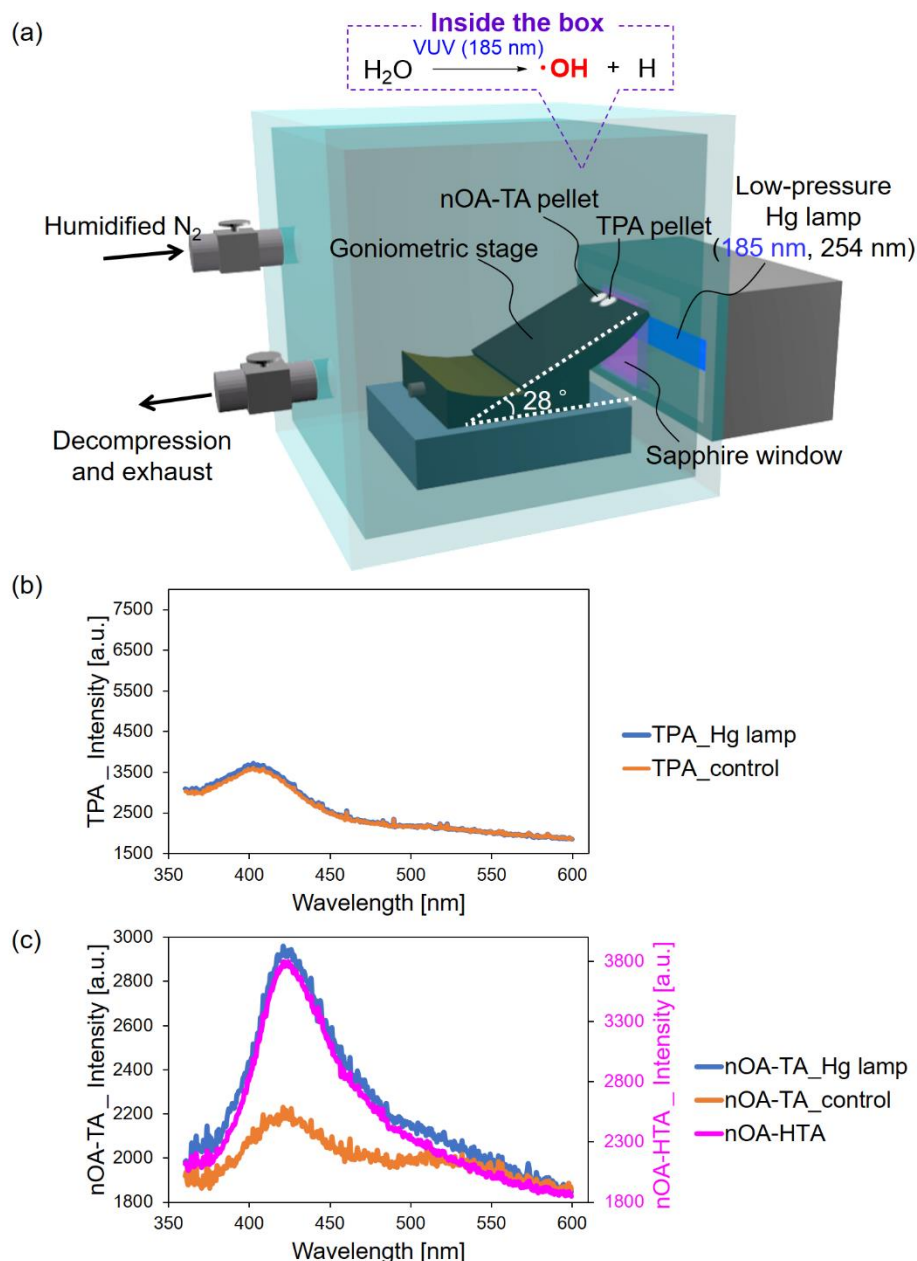


Figure 1-5. (a) Schematic diagram of the experimental system for exposing $\cdot\text{OH}$ radicals generated by low-pressure Hg lamp irradiation of pellets. (b) Fluorescence spectra of DMSO solution of TPA. Excitation at 310 nm. (c) Fluorescence spectra of DMSO solutions of nOA-TA and nOA-HTA. Excitation at 310 nm.

irradiation with the low-pressure Hg lamp. If high concentrations of ozone of several tens of ppm or more were generated, there was concern about the effect of degradation and decomposition of nOA-TA. The ozone concentration in the box after 2 hours irradiation of the low-pressure Hg lamp was measured with an ozone detector tube (Gastec, No. 18 L), and found to be 0.025 ppm or less.

As a control, pellets prepared in the same manner were left in a nitrogen atmosphere of the same humidity for 2 hours without exposure to the low-pressure Hg lamp.

After 2 h treatment, each pellet was dissolved in DMSO to a concentration of 1.7×10^{-2} mol/L for the TPA solution and 4.7×10^{-3} mol/L for the nOA-TA solution. The solution was transferred to a fluorescence cuvette and the fluorescence spectrum was measured with excitation light at 310 nm. Bis (*n*-octylammonium) hydroxyterephthalate (nOA-HTA) was synthesized by replacing TA with HTA and the fluorescence spectrum of its 7.9×10^{-8} mol/L DMSO solution was also taken.

The fluorescence spectrum of the solution of TPA irradiated with the low-pressure Hg lamp was almost the same as that of the solution of the control TPA not irradiated with the low-pressure Hg lamp (Figure 1-5b). On the other hand, the fluorescence spectrum of the solution of nOA-TA irradiated with the Hg lamp had a clear peak around 423 nm, the same as the solution of nOA-HTA. Its fluorescence intensity was greater than that of the solution of the control nOA-TA which was not irradiated with the low-pressure Hg lamp (Figure 1-5c).

From the above results, it is suggested that some of the TA in the nOA-TA crystals reacted with $\cdot\text{OH}$ generated by irradiation of the low-pressure Hg lamp to form HTA, and the fluorescence of the DMSO solution increased at around 423 nm.

In the crystal of nOA-TA, there were zero-dimensional voids around the terephthalates (Figure 1-4c). Due to the presence of these voids, gaseous $\cdot\text{OH}$ penetrated into the crystal and reacted with TA to form HTA, which exhibited fluorescence response functions. On the other hand, as there were no such voids in the crystal of TPA, the penetration of the $\cdot\text{OH}$ into the crystal and the reaction with TPA was suppressed, and no fluorescence change occurred.

1.3.3. Immobilization of nOA-TA on a porous sheet

nOA-TA was dissolved in methanol and adjusted to a concentration of 0.12 mol/L. A membrane filter made of hydrophilic polytetrafluoroethylene (ADVANTEC, H020 A047 A) was immersed in the solution, and the solution was retained in the pores of the membrane filter. The immersed membrane filter was removed from the solution, dried under reduced pressure for 1 hour, and subjected to powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). The main peaks of the PXRD pattern of the membrane filter after immersion and drying were in good agreement with that of the PXRD pattern predicted from the nOA-TA crystal structure (Figure 1-6). The SEM image indicated that particulate solids with grain sizes around 100 nm were immobilized between the fibers of the membrane filter (Figure 1-7). Thus, crystals of the organic salt with the same structure as that of nOA-TA were successfully immobilized on the membrane filter.

The author used this nOA-TA immobilized sheet for subsequent experiments and described the measurement of the spatial distribution of $\cdot\text{OH}$ generated by the low-pressure Hg lamp.

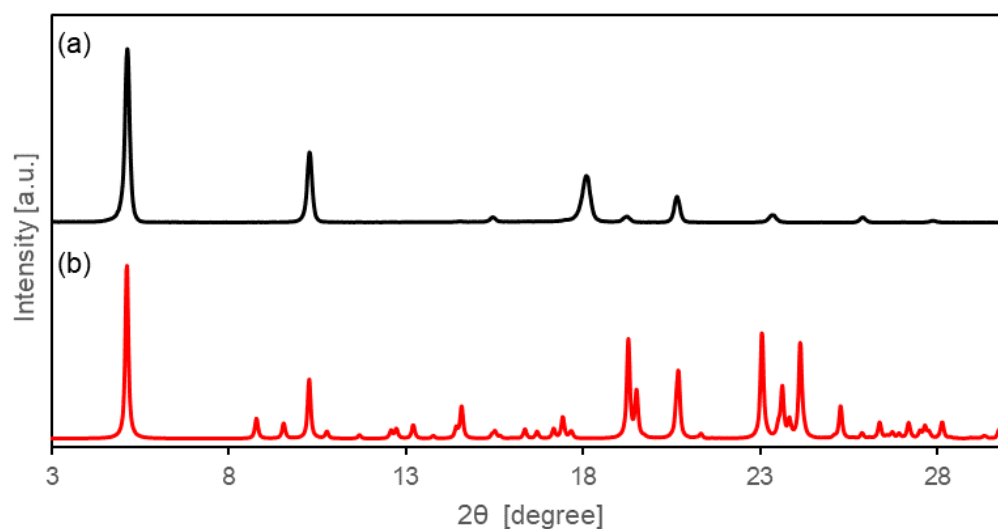


Figure 1-6. (a) PXRD pattern of the membrane filter after immersion and drying. (b) PXRD pattern predicted from the nOA-TA crystal structure.

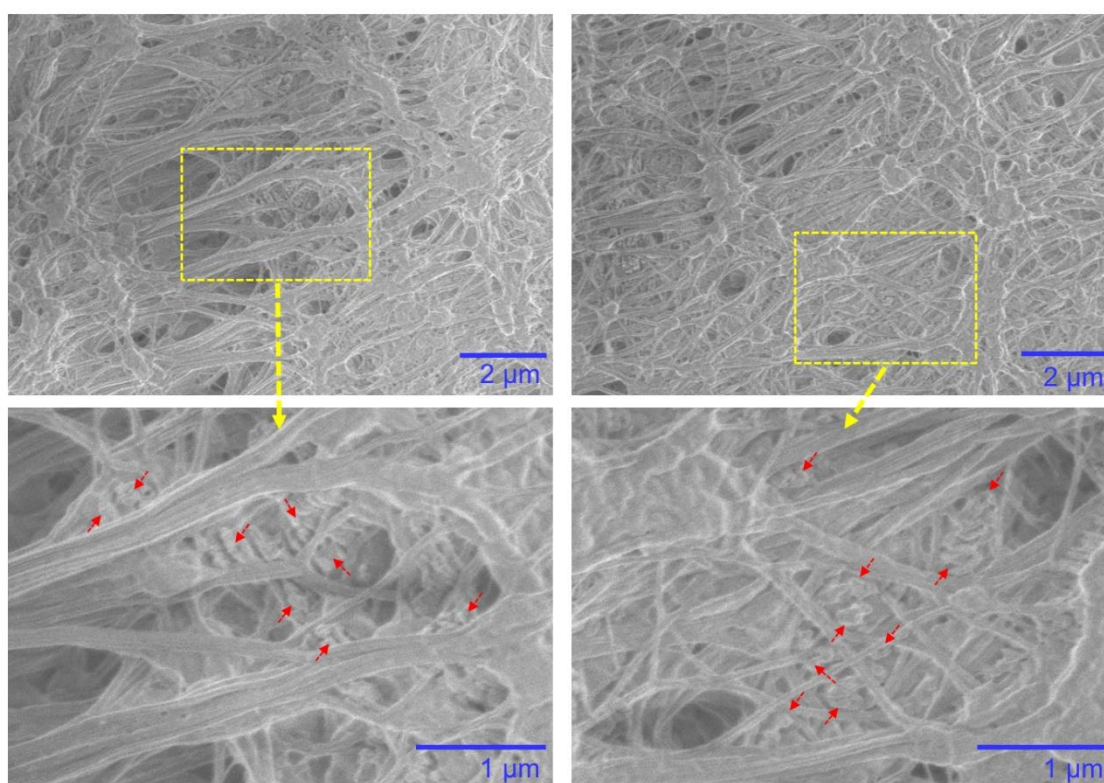


Figure 1-7. SEM images of the membrane filter after immersion and drying. The red arrows indicate the nOA-TA crystals immobilized between the fibers of the membrane filter.

1.3.4 Detection of $\cdot\text{OH}$ with the nOA-TA immobilized sheet

Figure 1-8a shows the experimental system used. The goniometric stage was placed in the acrylic box with the sapphire window in the same arrangement as described in Figure 1-5a. The nOA-TA

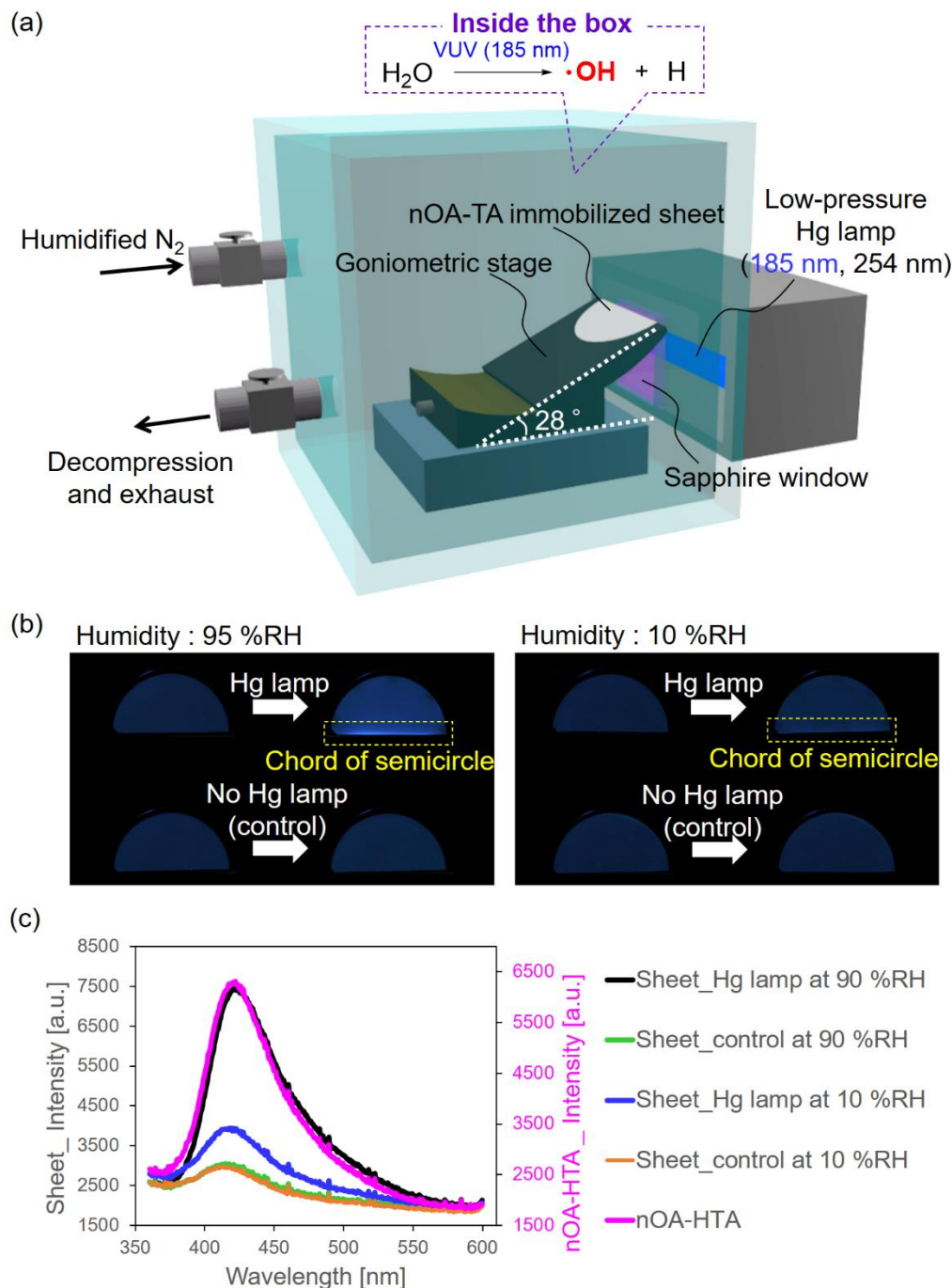


Figure 1-8. (a) Schematic diagram of an experimental system for exposing $\cdot\text{OH}$ radicals generated by low-pressure Hg lamp irradiation to nOA-TA immobilized sheet. (b) Fluorescent images of nOA-TA immobilized sheets under 313 nm light irradiation. Humidity in the nitrogen atmosphere was 95 %RH (left) and 10 %RH (right). (c) Fluorescence spectra of methanol eluate of nOA-TA immobilized sheets and methanol solution of nOA-HTA. Excitation at 310 nm.

immobilized sheet was cut into a semicircle, and placed on the inclined surface of the stage so that the chord of the semicircle coincided with the highest side of the slope. The inside of the acrylic box was depressurized to remove oxygen to a concentration of about 0.2 %, and humidified nitrogen was passed through to adjust the humidity to 95 %RH or 10 %RH. The low-pressure Hg lamp was irradiated through the sapphire window of the acrylic box for 2 hours, and gaseous $\cdot\text{OH}$ was generated and exposed to the sheet. The ozone concentration in the box after 2 hours of irradiation of the low-pressure Hg lamp was measured in the same manner as described above, and found to be 0.025 ppm or less. As a control, an nOA-TA immobilized sheet prepared in the same manner was left in a nitrogen atmosphere of the same humidity for 2 hours without exposure to the low-pressure Hg lamp.

Fluorescent images (excitation wavelength: 313 nm) of the sheets before and after the 2-hour treatment are shown in Figure 1-8b. The fluorescence intensity increased after exposure to the low-pressure Hg lamp, and this tendency was more pronounced under high relative humidity. Furthermore, the distribution of strong fluorescence intensity was observed especially near the chord. The control sheets, which were left for 2 hours in a nitrogen atmosphere of the same humidity without exposure to the low-pressure Hg lamp, showed no change in fluorescence.

Each of the four sheets was immersed in 1 mL of methanol after the 2 hour treatment to elute the immobilized nOA-TA. The eluate was transferred to a fluorescence cuvette and the fluorescence spectrum was measured with excitation light at 310 nm. A methanol solution of nOA-HTA was prepared at a concentration of 1.6×10^{-7} mol/L and the fluorescence spectrum measured upon excitation at 310 nm was also taken. The fluorescence spectra of the methanol eluate of the sheets, which were irradiated with the low-pressure Hg lamp, and the methanol solution of nOA-HTA had a peak at the same position, around 420 nm. The fluorescence intensities of each eluent were in the following order: Hg lamp irradiation at 95 %RH > Hg lamp irradiation at 10 %RH > no Hg lamp irradiation at 10 or 95 %RH (Figure 1-8c).

From the above results, it is suggested that some of the TA in the nOA-TA crystals immobilized on the sheets reacted with $\cdot\text{OH}$ generated by irradiation of the low-pressure Hg lamp to form HTA, which caused an increase in the fluorescence of the methanol eluate around 420 nm. The remarkably strong fluorescence at 95 %RH is thought to be due to the fact that the amount of water molecules decomposed by VUV light to form $\cdot\text{OH}$ was greater at 95 %RH than at 10 %RH.

Methanol solutions of several known concentrations of nOA-HTA were prepared and calibration curve showing the relationship between their fluorescence intensities and concentrations was obtained. Using this calibration curve, the weight of nOA-HTA was determined from the fluorescence intensity of the eluate. Similarly, several known concentrations of nOA-TA in methanol were prepared, and a calibration curve showing the relationship between their absorbance at 238.5 nm and their concentration was obtained. Using this calibration curve, the weight of nOA-TA was determined from

the absorbance at 238.5 nm of the eluate. (As the ratio of nOA-HTA to nOA-TA in the eluate was less than 0.01, the effect on the absorbance of nOA-HTA was negligible.)

Finally, the conversion rates of TA to HTA were calculated to be 4.8×10^{-5} for Hg lamp irradiation at 95 %RH, 1.2×10^{-5} for Hg lamp irradiation at 10 %RH, 2.8×10^{-6} and 1.7×10^{-6} without Hg lamp irradiation at 95 %RH and 10 %RH, respectively. (A series of experimental procedures for deriving the conversion rate are shown in Figure 1-9.)

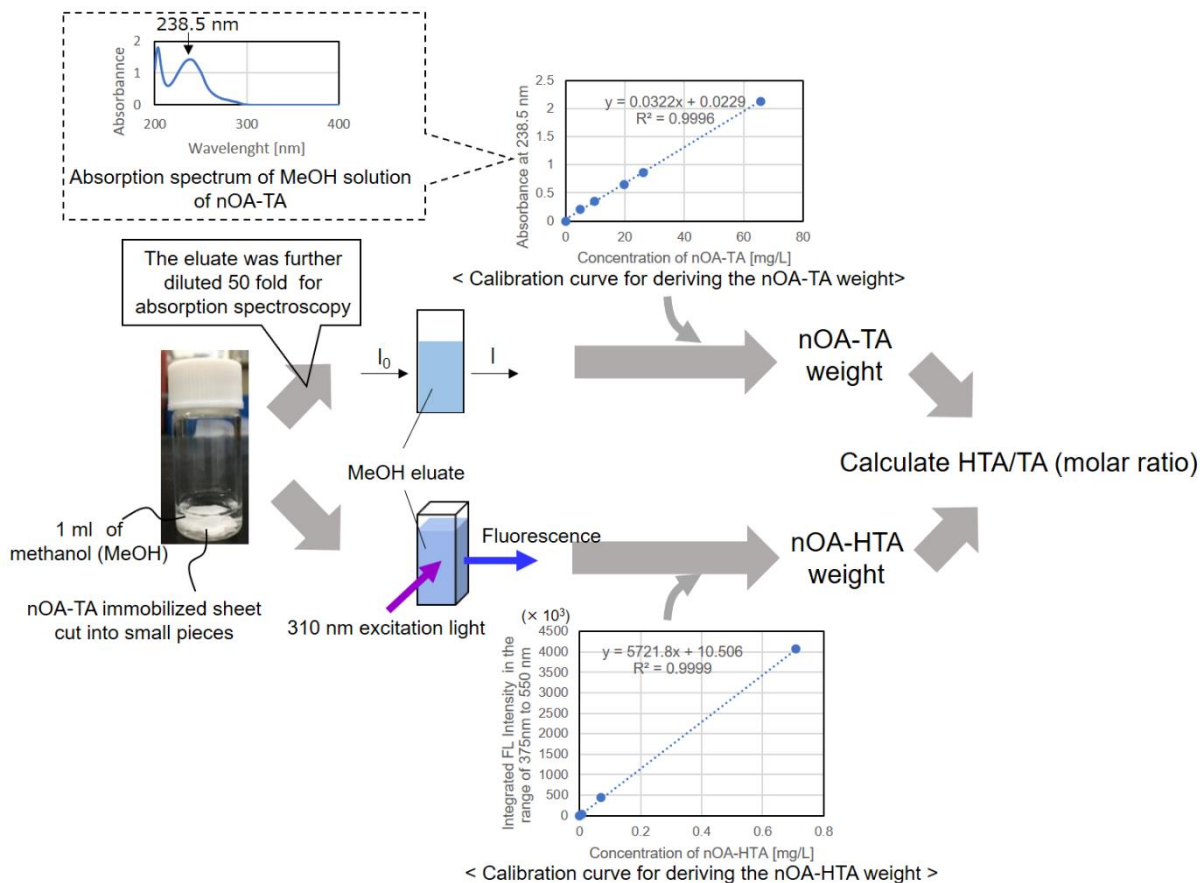


Figure 1-9. Procedure for deriving conversion rate of TA to HTA.

In the fluorescence image of Figure 1-8b, the increased fluorescence of the sheet after Hg lamp irradiation may also be due to the formation of HTA. Since the chord of the semicircle was close to the sapphire window, the intensity of the incident VUV, which decomposed water molecules to form $\cdot\text{OH}$, was particularly strong around the chord, and it is considered that a strong fluorescence distribution was observed due to the local formation of HTA near the chord. In this way, it was confirmed that the distribution of $\cdot\text{OH}$ in the space could be visualized by using the nOA-TA immobilized sheet.

Incidentally, a separate experiment was carried out in which the nOA-TA immobilized sheet was exposed to ozone at a concentration of 4 ppm for 4 hours, and the fluorescence did not change (Figure

1-10). Ozone did not produce HTA, and no change in fluorescence was observed. Therefore, the increase in fluorescence with Hg lamp irradiation, as seen in Figure 1-8b, was due to $\cdot\text{OH}$ and not ozone.

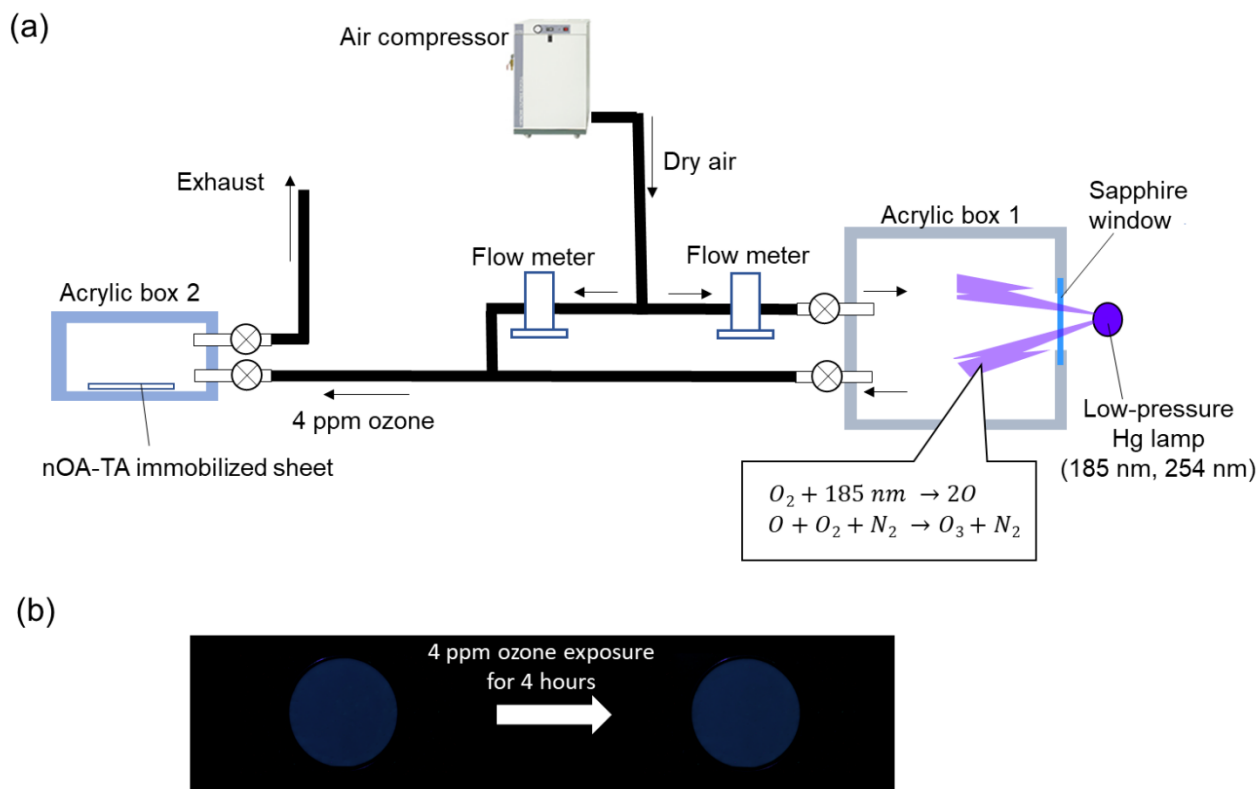


Figure 1-10. (a) Schematic diagram of an experimental system for exposing nOA-TA immobilized sheet to ozone. (b) Fluorescence photographs of nOA-TA immobilized sheet before and after 4 ppm ozone exposure for 4 hours. Excitation wavelength was 313 nm.

1.4 Conclusion

The author prepared *n*-alkylammonium terephthalate salts with various alkyl chain lengths. When the alkyl chain length was greater than 8, the organic salt adopted a crystal structure in which the alkyl chains were arranged parallel to each other and the zero-dimensional voids were adjacent to TA. This parallel arrangement of alkyl chains acted as a hydrophobic block and exhibited high water vapor resistance.

The highly hydrophobic nOA-TA crystal powder was exposed to $\cdot\text{OH}$ generated by the low-pressure Hg lamp method and a fluorescence response was observed, indicating the formation of HTA. Due to the presence of the zero-dimensional voids, gaseous $\cdot\text{OH}$ penetrated into the crystal and reacted with TA to form fluorescent HTA, allowing $\cdot\text{OH}$ to be detected.

Furthermore, the author successfully immobilized nOA-TA crystals uniformly in the pores of the membrane filter and confirmed that the spatial distribution of $\cdot\text{OH}$ could be evaluated by using this sheet.

From these results, the author believes that *n*-alkylammonium terephthalate with alkyl chain lengths greater than 8, such as nOA-TA, is an ideal solid scavenger of $\cdot\text{OH}$ and the nOA-TA immobilized sheet is applicable to on-site $\cdot\text{OH}$ measurements of various processes.

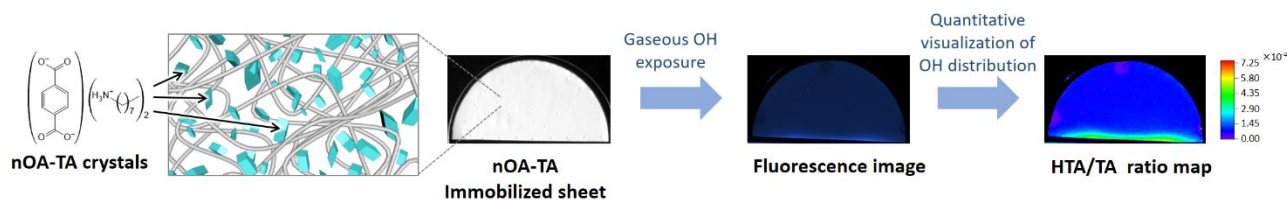
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Chapter 2

Investigation of Response Enhancement and Quantification of Gaseous OH Radical Measurement Using *n*-Alkylammonium Terephthalate Immobilized Sheet



Abstract: As described in Chapter 1, *n*-alkylammonium terephthalate immobilized sheets enable the facile measurement of gaseous OH radical ($\cdot\text{OH}$). This chapter describes the preparation conditions of the sheets to further improve the detection performance of $\cdot\text{OH}$. The fluorescence response to $\cdot\text{OH}$ tended to increase with shorter alkyl chain lengths of the *n*-alkylamines, with bis(*n*-octylammonium) terephthalate (nOA-TA), an organic salt with an alkyl chain length of 8, exhibiting the best response performance. Furthermore, the smaller the pore size of the membrane filter immobilizing nOA-TA, the better the fluorescence response performance to $\cdot\text{OH}$. Finally, the author developed a procedure for converting the fluorescence image of the nOA-TA immobilized sheet exposed to gaseous $\cdot\text{OH}$ into an HTA/TA ratio map. This makes it possible to quantitatively visualize the spatial distribution of gaseous $\cdot\text{OH}$ two-dimensionally.

2.1 Introduction

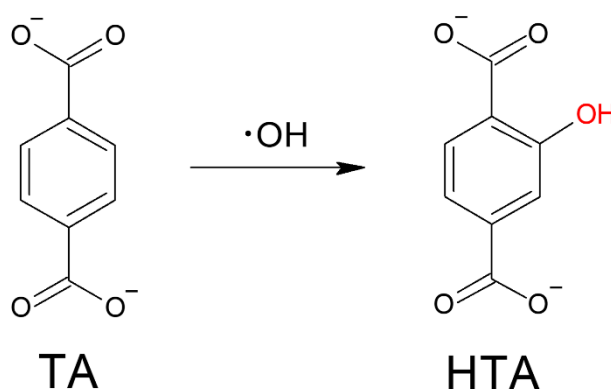
Reactive oxygen species is a general term for oxygen-derived chemical species with high chemical reactivity, such as OH radical ($\cdot\text{OH}$), superoxide anion radical ($\cdot\text{O}_2^-$), hydroperoxyl radical ($\text{HOO}\cdot$), and hydrogen peroxide (H_2O_2). $\cdot\text{OH}$, in particular, has extremely high oxidizing power and is widely used for the treatment of solid surfaces and air purification. $\cdot\text{OH}$ is generated from vacuum ultraviolet (VUV) light,^[1] plasma systems,^[2] and photocatalysts.^[3] Therefore, a method of monitoring $\cdot\text{OH}$ has been desired in order to control the amount of $\cdot\text{OH}$ generated from such processes. However, because of its high reactivity and short lifetime of microseconds to milliseconds, methods for measuring gaseous $\cdot\text{OH}$ are very limited.

The laser-induced fluorescence (LIF) method, which measures fluorescence emission associated with electronic excitation and de-excitation of $\cdot\text{OH}$ by laser beam irradiation, is known as a method for directly measuring gaseous $\cdot\text{OH}$,^[4] but it is not suitable for on-site measurements due to the large size and lack of portability of the instrument.

In electron spin resonance (ESR) spectroscopy, the spin-trapping agent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) reacts with $\cdot\text{OH}$ in aqueous solution to form stable organic radicals. The ESR spectrum is used to indirectly measure $\cdot\text{OH}$.^[5] However, DMPO is itself unstable when exposed to oxygen and light, and it has many handling restrictions, making it unsuitable as a method for measuring gaseous $\cdot\text{OH}$.

Iwamori et al. reported a method for detecting $\cdot\text{OH}$ from decolorization of methylene blue dye by a degradation reaction using a Nafion film, but there are serious shortcomings in the uniformity of the detection film.^[6]

Terephthalate (TA) reacts with $\cdot\text{OH}$ to form hydroxyterephthalate (HTA), and $\cdot\text{OH}$ can be measured indirectly from the fluorescence of HTA at around 420 nm (Scheme 2-1).^[7] Other common reactive oxygen species ($\cdot\text{O}_2^-$, $\text{HOO}\cdot$, H_2O_2) have been reported not to interfere with $\cdot\text{OH}$ in its reaction with TA.^[8] Kanazawa et al. reported the detection of gaseous $\cdot\text{OH}$ generated by non-thermal plasmas using agarose-based hydrogel sheets containing TA.^[9] However, these hydrogel sheets are water-containing and are susceptible to drying, resulting in poor shelf life.



Scheme 2-1. Formation of HTA via the reaction of TA with $\cdot\text{OH}$.

In Chapter 1, the author reported that *n*-alkylammonium terephthalate, an organic salt composed of terephthalic acid (TPA) and primary *n*-alkylamine, can serve as a solid $\cdot\text{OH}$ scavenger and detect

gaseous $\cdot\text{OH}$. When the alkyl chain length of the *n*-alkylamine used was 8 or longer, the author found that a crystal structure was formed in which the alkyl chains were aligned parallel to each other, and furthermore, zero-dimensional voids existed in the vicinity of the TA. This parallel alignment of alkyl chains played the role of hydrophobic blocks and exhibited excellent moisture resistance. When highly hydrophobic bis(*n*-octylammonium) terephthalate (nOA-TA) crystal powder was exposed to gaseous $\cdot\text{OH}$ generated by a low-pressure mercury (Hg) lamp, a fluorescence response suggestive of HTA formation was observed. It was strongly suggested that the presence of zero-dimensional voids allows $\cdot\text{OH}$ to penetrate into the interior of the crystal and react with TA to form fluorescent HTA. Furthermore, the author succeeded in immobilizing nOA-TA nanocrystals uniformly on a membrane filter by a simple dipping and drying process, and demonstrated that the spatial distribution of gaseous $\cdot\text{OH}$ can be visualized as the HTA fluorescence intensity distribution by using this sheet as an $\cdot\text{OH}$ detection sheet.^[10]

The author believes that *n*-alkylammonium terephthalates with alkyl chain lengths longer than 8, such as nOA-TA, are ideal solid scavengers for gaseous $\cdot\text{OH}$ because of their high moisture resistance. The sheets on which they are immobilized are easily fabricated and highly portable, enabling application for on-site $\cdot\text{OH}$ measurements in various processes. In addition, these sheets are non-water-containing, so they are resistant to drying and have excellent shelf life.

With the aim of practical application of the $\cdot\text{OH}$ measurement method of our study described in Chapter 1, the author herein performed a more detailed verification of the $\cdot\text{OH}$ detection principle and fluorescence response performance of this method. First, in order to demonstrate the effectiveness of the $\cdot\text{OH}$ measurement method using *n*-alkylammonium terephthalate immobilized sheets, more solid evidence of HTA formation by $\cdot\text{OH}$ exposure was provided by high-sensitivity mass spectrometry. The author also confirmed that the amount of fluorescence response due to HTA formation was dependent on $\cdot\text{OH}$ exposure time. To enhance the fluorescence response performance to $\cdot\text{OH}$, the author evaluated the effects of the alkyl chain length of the *n*-alkylamine and the pore size of the membrane filter on the fluorescence response performance. Finally, for more quantitative visualization of the $\cdot\text{OH}$ distribution in space, the author developed a procedure to convert fluorescence images of the sheets after $\cdot\text{OH}$ exposure into maps of HTA/TA ratio.

2.2 Experimental section

2.2.1 Synthesis of organic salts

All chemicals and solvents were commercially available and used without any purification. *n*-Alkylamines with alkyl chain lengths of 8, 9, and 10 carbons were mixed with TPA in methanol at a molar ratio of 2:1, and the methanol was evaporated to yield crystal powders of bis(*n*-octylammonium) terephthalate nOA-TA, bis(*n*-nonylammonium) terephthalate (nNA-TA) and bis(*n*-decylammonium)

terephthalate (nDA-TA) crystal (Figure 2-1a). Bis(*n*-octylammonium) hydroxy terephthalate (nOA-HTA) was synthesized in the same way, substituting HTA for TA (Figure 2-1b).

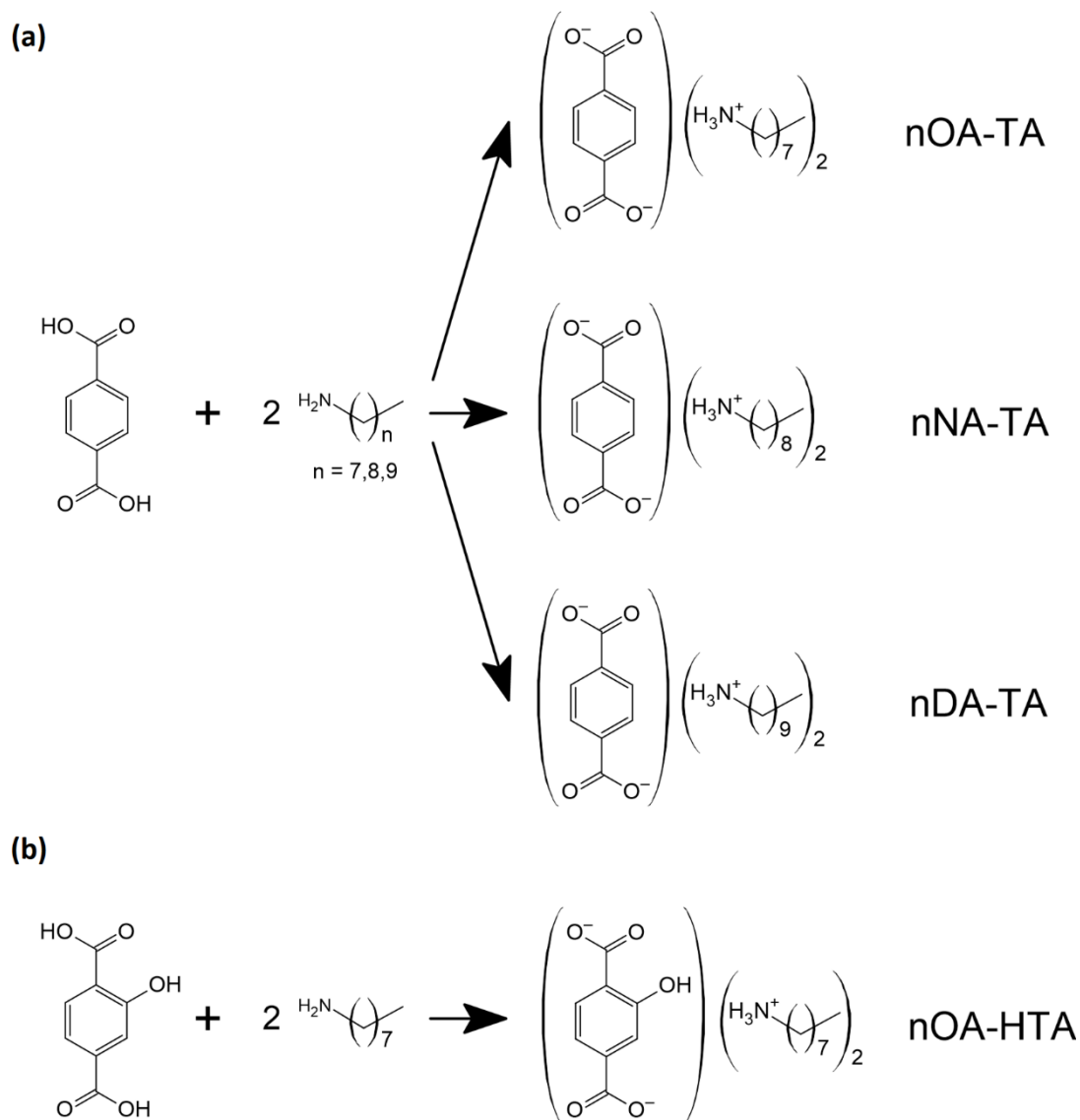


Figure 2-1. (a) Organic salts composed of TPA and *n*-alkylamines. (b) Organic salt composed of 2-hydroxyterephthalic acid and *n*-octylamine.

2.2.2 Preparation of organic salt-immobilized sheet

Figure 2-2 shows the procedure for preparing organic salt-immobilized sheets. The synthesized organic salt powders (nOA-TA, nNA-TA, nDA-TA) were dissolved in methanol and adjusted to a concentration of 0.12 mol/L. Hydrophilic polytetrafluoroethylene (PTFE) membrane filters with pore sizes of 0.1 μm , 0.2 μm , and 0.5 μm (H010A047A, H020A047A, and H050A047A from ADVANTEC) were immersed in the prepared solution for 5 minutes while the solution flowed into the pores of the membrane filters. The immersed membrane filters were removed from the solution

and dried under reduced pressure for 1 hour. The amount of organic salt immobilized on the sheet was determined from the weight change of the sheet before and after immersion in the solution.

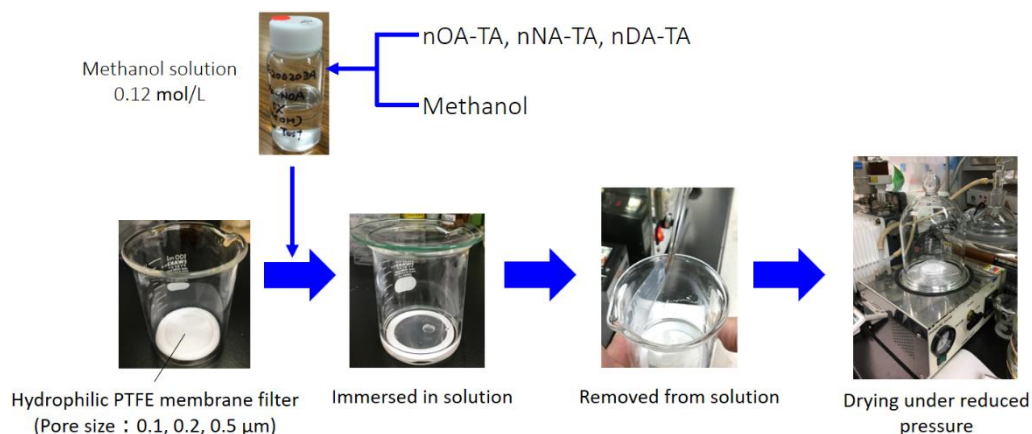


Figure 2-2. Procedure for preparing organic salt-immobilized sheets.

2.2.3 Preparation of nOA-TA immobilized sheets with trace amounts of nOA-HTA

Figure 2-3 shows the procedure for preparing nOA-TA immobilized sheets with trace amounts of nOA-HTA. First, a methanol solution of nOA-TA was prepared at a concentration of 0.12 mol/L. A small amount of nOA-HTA was dissolved in the methanol solution of nOA-TA, and the molar ratio of nOA-HTA to nOA-TA in the methanol solution was adjusted to 5.92×10^{-5} , 2.96×10^{-4} , 5.92×10^{-4} and 7.04×10^{-4} . Hydrophilic PTFE membrane filters with a pore size of 0.1 μm were immersed in each nOA-HTA/nOA-TA mixed methanol solution for 5 minutes to retain the solution in the pores of the membrane filters. The immersed membrane filters were removed from the solution and dried under reduced pressure for 1 hour.

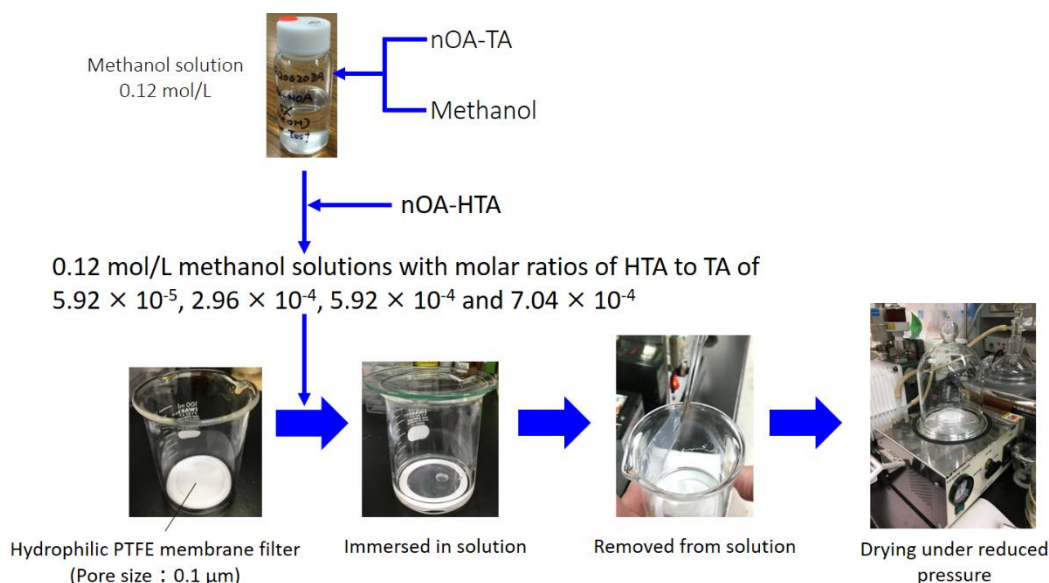


Figure 2-3. Procedure for preparation of nOA-TA immobilized sheets with trace amounts of nOA-HTA.

2.2.4 ·OH exposure experiment using low-pressure Hg lamp method

·OH exposure experiments using the low-pressure Hg lamp method were performed using almost the same experimental system as described in Chapter 1.^[10] A detailed experimental system is shown in Figure 2-4.

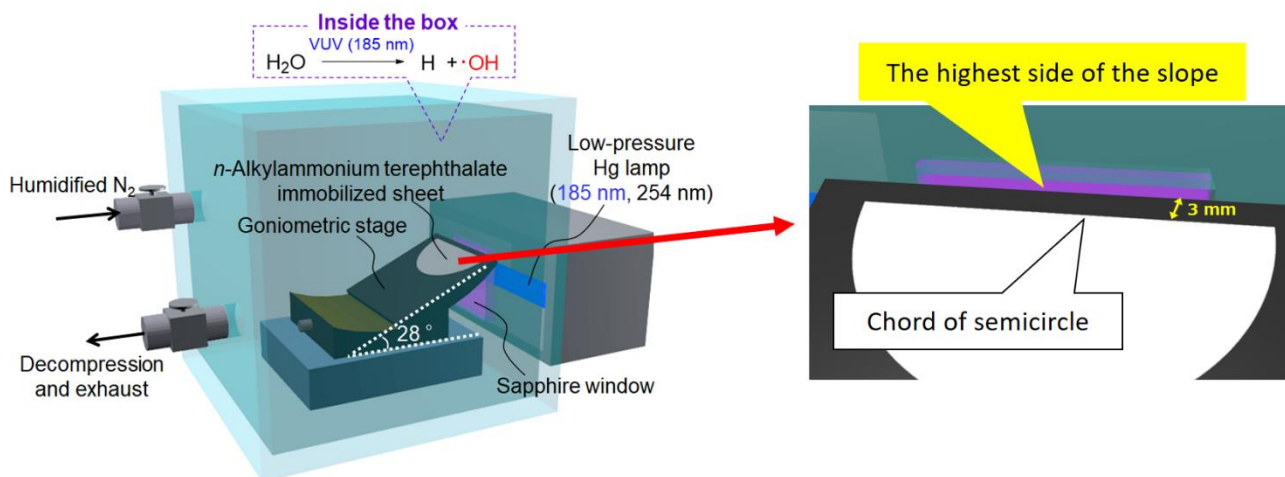


Figure 2-4. Schematic diagram of an experimental system for exposing ·OH generated by low-pressure Hg lamp irradiation to *n*-alkylammonium terephthalate immobilized sheet.

2.2.5 Electrospray ionization mass spectrometry (ESI-MS) analysis

A sample solution diluted with methanol was infused at a flow rate of 5 $\mu\text{L min}^{-1}$ into an LTQ Orbitrap XL mass spectrometer (Thermo Fisher Scientific, Inc.) and ionized by ESI in the negative ion mode. The spray voltage was set at 3 kV.

2.2.6 Powder X-ray diffraction analysis

Powder X-ray diffraction (PXRD) patterns were measured by using a Rigaku Ultima IV with graphite-monochromatized Cu K α radiation ($\lambda = 1.54187 \text{ \AA}$) at room temperature.

2.2.7 Fluorescence spectroscopy measurements

Fluorescence spectra were measured with 310 nm excitation light from an LED source (Ocean Optics, LLS-310) and a spectrograph equipped with a charge coupled device (CCD) detector (Andor Technology, Shamrock SR-303i). A detailed measurement system is shown in Figure 2-5 right.

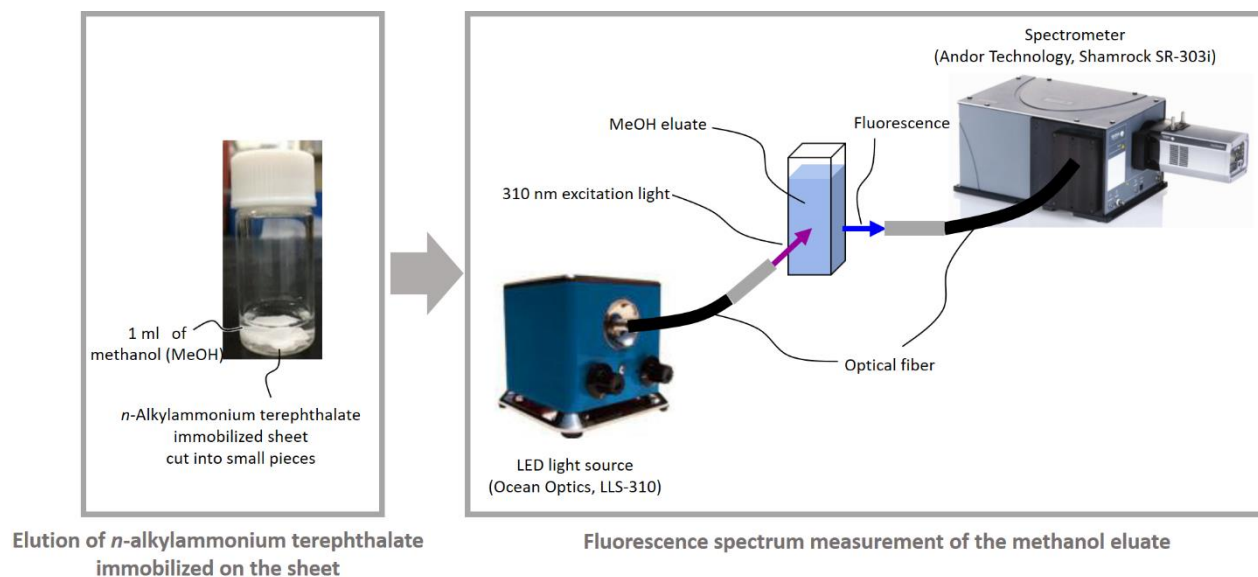


Figure 2-5. Elution of *n*-alkylammonium terephthalate immobilized on the sheet (left) and measurement of the fluorescence spectrum of the eluate (right).

2.2.8 Fluorescence image acquisition

Fluorescence images were taken with irradiation of 313 nm light from a 250 W mercury light source (Asahi Spectra, REX-250). A detailed measurement system is shown in Figure 2-6.

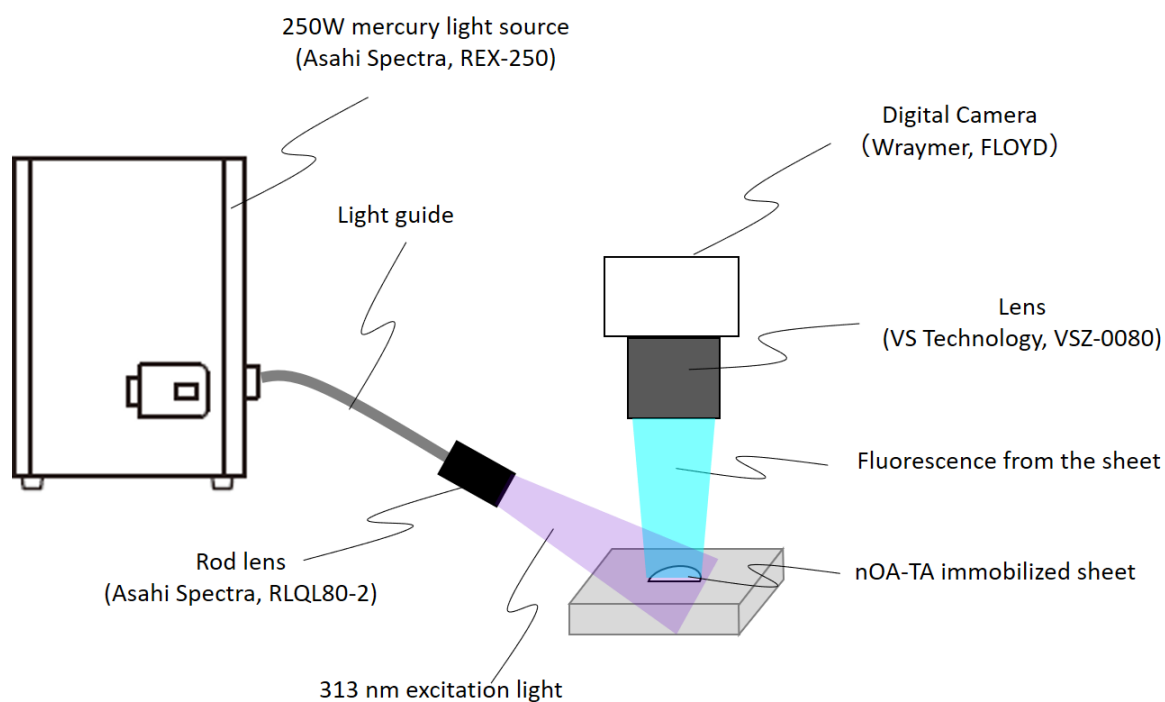


Figure 2-6. Schematic diagram of an experimental system for fluorescence image acquisition.

2.3 Results and Discussion

2.3.1 Verification of crystal structures of organic salt-immobilized sheets

PXRD patterns of the prepared organic salt powders and the organic salt-immobilized sheets (membrane filter pore size: 0.2 μm) are shown in Figure 2-7. The main PXRD peaks of the nOA-TA immobilized sheet were in good agreement with those of nOA-TA powder, indicating that crystals with the same structure as nOA-TA powder were immobilized on the membrane filter (Figure 2-7a). It was confirmed that nNA-TA and nDA-TA crystals were successfully immobilized on the membrane filter as well (Figure 2-7b and 7c).

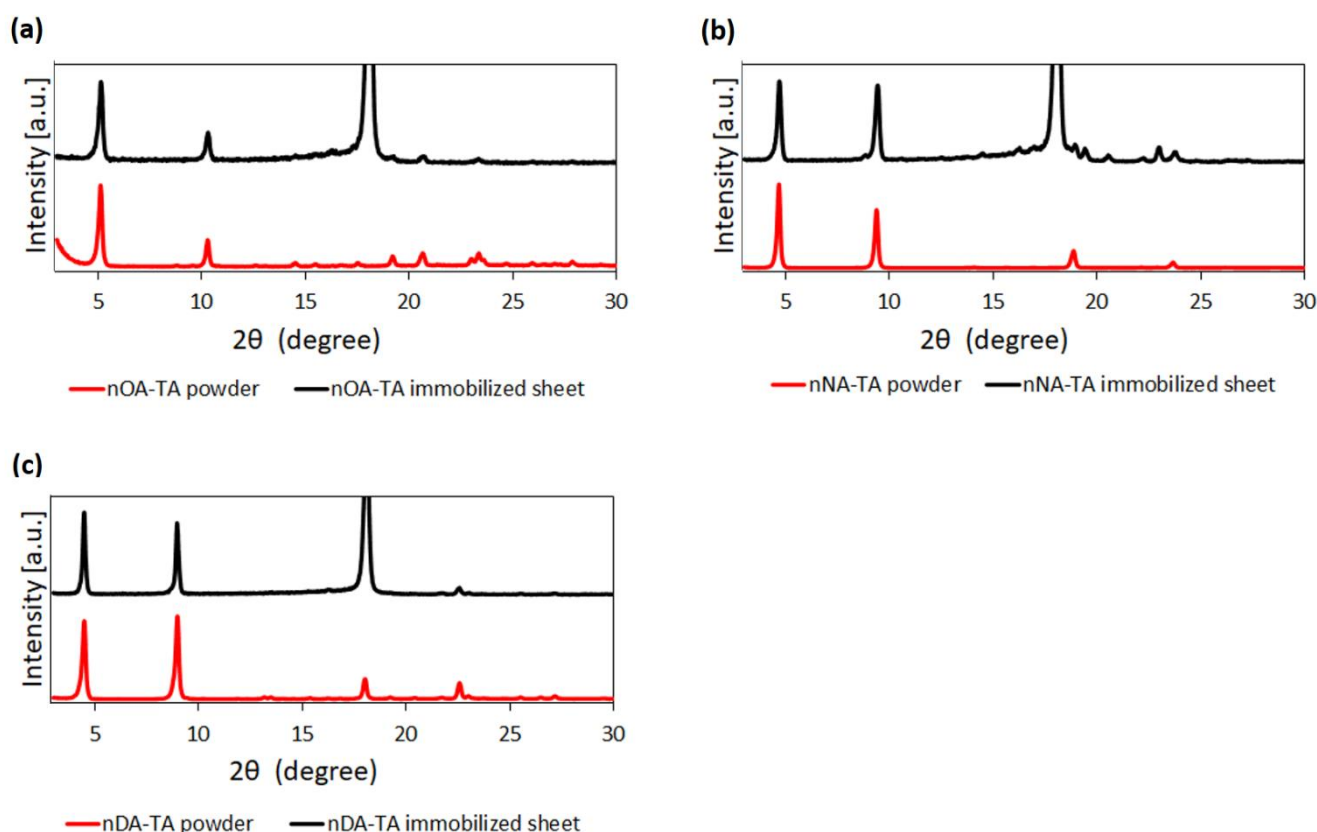


Figure 2-7. (a) PXRD patterns of nOA-TA immobilized sheet (black line) and nOA-TA powder (red line). (b) PXRD patterns of nNA-TA immobilized sheet (black line) and nNA-TA powder (red line). (c) PXRD patterns of nDA-TA immobilized sheet (black line) and nDA-TA powder (red line).

2.3.2 Verification of the formation of HTA by exposure of gaseous $\cdot\text{OH}$ to nOA-TA immobilized sheet

The nOA-TA immobilized sheet (membrane filter pore size: 0.2 μm) was exposed to $\cdot\text{OH}$ for 4 hours using the low-pressure Hg lamp method, and then immersed in 1 mL of methanol to elute the

immobilized nOA-TA (Figure 2-5, left). The eluate was transferred to a fluorescence cuvette and the fluorescence spectrum was measured with excitation light at 310 nm. A methanol solution of nOA-HTA was prepared at a concentration of 7.7×10^{-7} mol/L and the fluorescence spectrum upon excitation at 310 nm was also measured. The fluorescence spectra of the methanol eluate of the sheet and the methanol solution of nOA-HTA had peaks at the same position, around 423 nm (Figure 2-8).

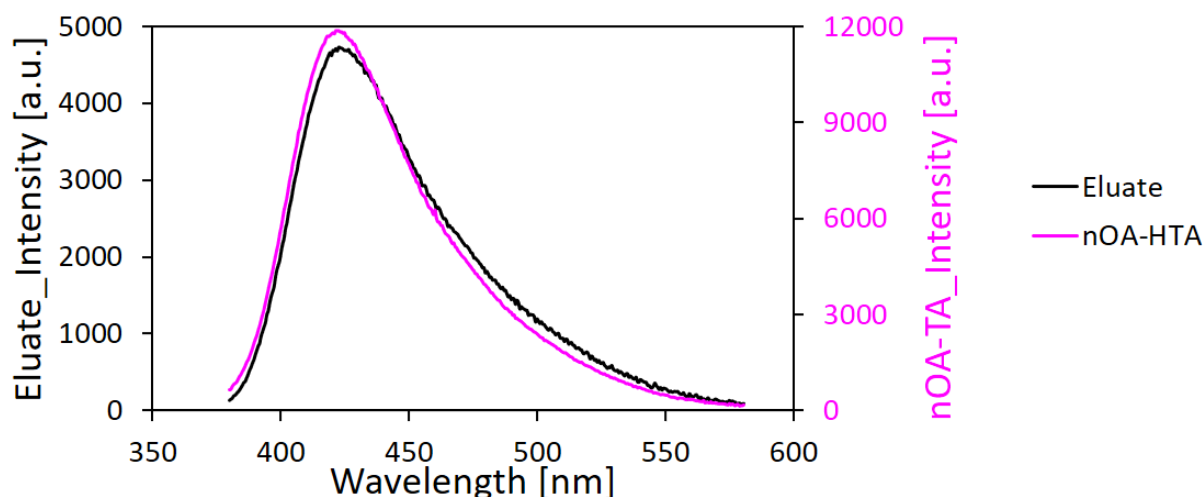


Figure 2-8. Fluorescence spectra of methanol eluates of nOA-TA immobilized sheet and methanol solutions of nOA-HTA.

ESI-MS spectra were measured for a methanol solution of nOA-TA adjusted to 1.2×10^{-4} mol/L, a methanol solution of nOH-HTA adjusted to 2.3×10^{-5} mol/L, and a 50-fold dilution of the methanol eluate from the nOA-TA-immobilized sheet after $\cdot\text{OH}$ exposure. In the methanol solutions of nOA-TA and nOA-HTA, m/z 165 and m/z 181 derived from TA and HTA, respectively, were identified as the base peaks (Figure 2-9a and 9b). In the methanol eluate from the nOA-TA immobilized sheet after $\cdot\text{OH}$ exposure, a weak HTA-derived peak at m/z 181 was detected along with the main component, TA-derived m/z 165, confirming the presence of trace amounts of HTA in the eluate (Figure 2-9c). These results indicate that some of the TA in the nOA-TA crystals immobilized on the sheet reacted with $\cdot\text{OH}$ generated by the low-pressure Hg lamp method to form HTA, which was responsible for the fluorescence emission around 423 nm in the methanol eluate observed in Figure 2-8.

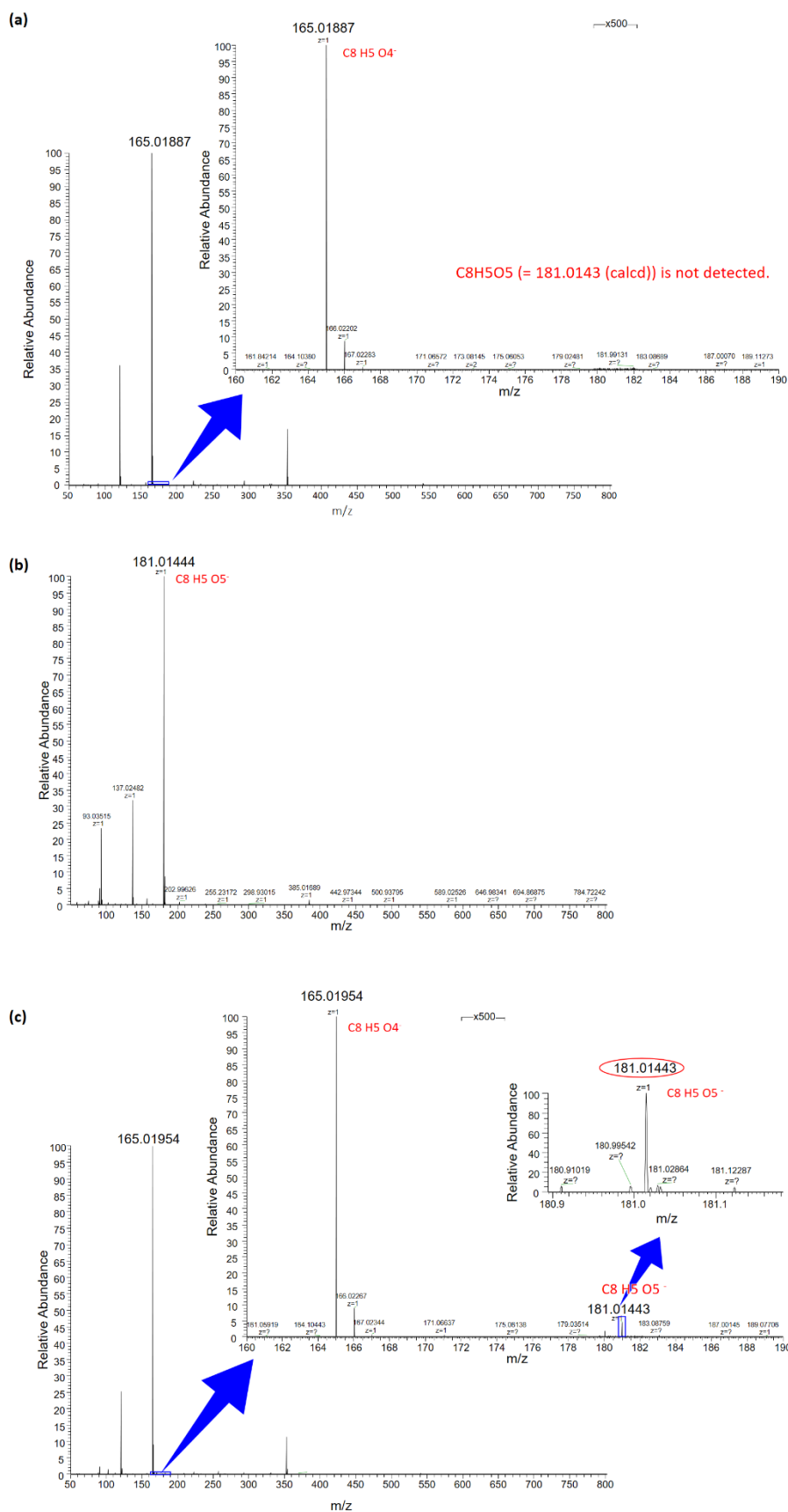


Figure 2-9. (a) Negative-ion ESI-MS of nOA-TA methanol solution. (b) Negative-ion ESI-MS of nOA-HTA methanol solution. (c) Negative-ion ESI-MS of methanol eluate of nOA-TA immobilized sheet.

2.3.3 Relationship between $\cdot\text{OH}$ exposure time and fluorescence response properties

Three nOA-TA immobilized sheets (membrane filter pore size: 0.2 μm) were exposed to $\cdot\text{OH}$ for 2, 3, and 4 hours, respectively, by the low-pressure Hg lamp method, and then immersed in 1 mL of methanol to elute the immobilized nOA-TA (Figure 2-5, left). Each eluate was transferred to a fluorescence cuvette and irradiated with 310 nm excitation light to obtain the fluorescence spectra shown in Figure 2-10a. The integral of the intensity of each fluorescence spectrum in the range of 400 to 450 nm was divided by the amount of each immobilized nOA-TA to obtain the value of n_a . The relationship between n_a and the exposure time of $\cdot\text{OH}$ is shown in Figure 2-10b. The n_a value increased with longer $\cdot\text{OH}$ exposure time. It is clear that as the $\cdot\text{OH}$ exposure time lengthened, the amount of HTA produced by the reaction of TA in the nOA-TA crystals immobilized on the sheet with $\cdot\text{OH}$ increased, resulting in higher n_a .

Incidentally, the increase in n_a slowed down from 3 to 4 hours of $\cdot\text{OH}$ exposure time (Figure 2-10b). Gaseous $\cdot\text{OH}$ is highly reactive and penetrates only near the surface of the sheets. Therefore, it is likely that the $\cdot\text{OH}$ exposure time was too long (4 hours) and the amount of nOA-TA crystals reacting with $\cdot\text{OH}$ near the surface of the sheet was insufficient, resulting in a slower increase in n_a .

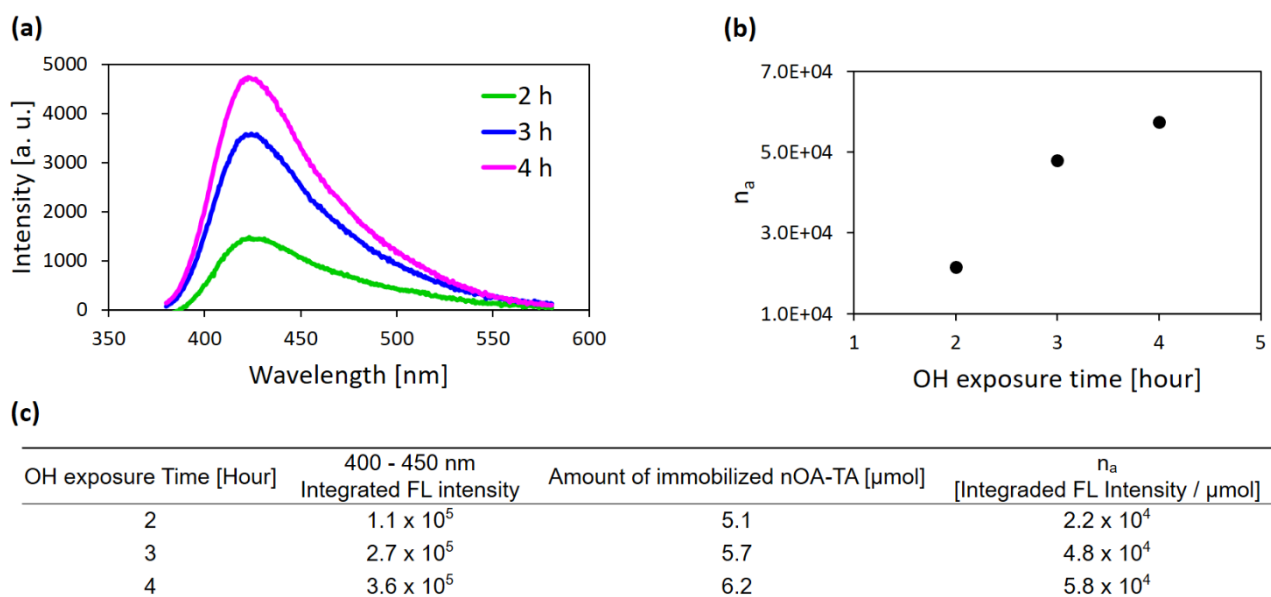


Figure 2-10. (a) Fluorescence spectra of methanol eluates of nOA-TA immobilized sheets at different $\cdot\text{OH}$ exposure times. (b) n_a versus $\cdot\text{OH}$ exposure time. (c) Table of integrated fluorescence (FL) intensity in the range of 400–450 nm, amount of nOA-TA immobilized on the sheets, and n_a .

2.3.4 Relationship between alkyl chain length and fluorescence response properties

The author investigated the dependence of the alkyl chain length of the *n*-alkylamines, which are the components of the *n*-alkylammonium terephthalate, on the fluorescence response performance to $\cdot\text{OH}$.

The nNA-TA immobilized sheet (alkyl chain length: 9; membrane filter pore size: 0.2 μm) and the nDA-TA immobilized sheet (alkyl chain length: 10; membrane filter pore size: 0.2 μm) were exposed to $\cdot\text{OH}$ for 2 hours by the low-pressure Hg lamp method. The immobilized nNA-TA and nDA-TA were eluted with methanol as described above, and the fluorescence spectrum of each eluate was measured with excitation light at 310 nm. The fluorescence spectra obtained are shown in Figure 2-11a, together with the fluorescence spectrum of the eluate of the nOA-TA immobilized sheet (alkyl chain length: 8; membrane filter pore size: 0.2 μm) in Figure 2-10a. All fluorescence spectra had a peak at approximately 423 nm, indicating that nNA-TA and nDA-TA, as well as nOA-TA, reacted with $\cdot\text{OH}$ generated by the low-pressure Hg lamp method to form HTA. The integral of the intensity of each fluorescence spectrum in the range of 400 to 450 nm was divided by the amount of each immobilized *n*-alkylammonium terephthalate to obtain the fluorescence response performance value n_b . As shown in Figure 2-11b, the n_b value decreased with longer alkyl chain length, resulting in the best fluorescence response performance to $\cdot\text{OH}$ for nOA-TA with a chain length of 8. In *n*-alkylammonium terephthalate crystals with alkyl chain lengths longer than 8, the alkyl chains are packed closely with all-*trans* zigzag conformations and aligned parallel to each other.^[10] Longer alkyl chain lengths enhance van der Waals interactions between alkyl chains, and thus strengthen the packing between them.^[11] It is likely that the stronger packing between alkyl chains limited the penetration of $\cdot\text{OH}$ into the crystal, and reduced the efficiency of the reaction of TA with $\cdot\text{OH}$ to form HTA, resulting in lower n_b .

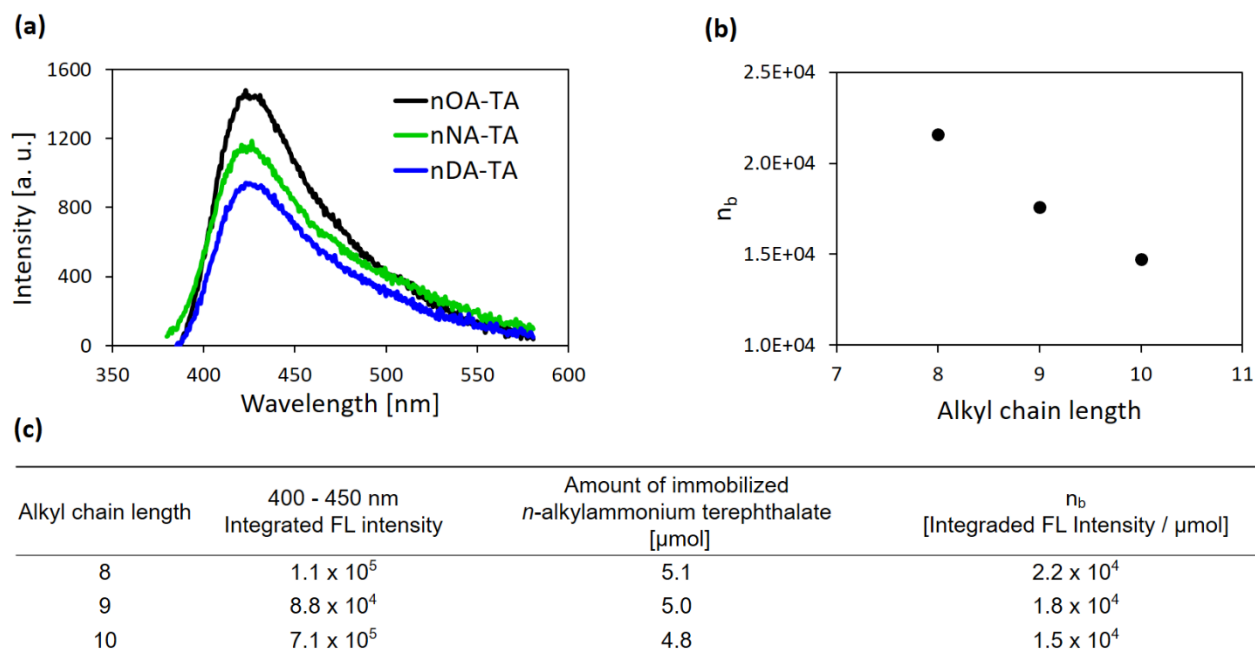


Figure 2-11. (a) Fluorescence spectra of methanol eluates of *n*-alkylammonium terephthalate (alkyl chain length: 8, 9, 10) immobilized sheets exposed to $\cdot\text{OH}$ for 2 h. (b) n_b versus alkyl chain length. (c) Table of integrated fluorescence (FL) intensity in the range of 400–450 nm, amount of *n*-alkylammonium terephthalate immobilized on the sheets, and n_b .

2.3.5 Relationship between membrane filter pore size and fluorescence response characteristics

The author next investigated the effect of membrane filter pore size on the fluorescence response performance to $\cdot\text{OH}$. The nOA-TA immobilized sheets (membrane filter pore size: 0.1 μm and 0.5 μm) were exposed to $\cdot\text{OH}$ for 2 hours by the low-pressure Hg lamp method. The nOA-TA immobilized on each sheet was eluted with methanol as described above, and the fluorescence spectrum of each eluate was measured with excitation light at 310 nm. The fluorescence spectra obtained are shown in Figure 2-12a, together with the fluorescence spectrum of the nOA-TA immobilized sheet prepared with the 0.2 μm pore size membrane filter of Figure 2-10a. The integral of the intensity of each fluorescence spectrum in the range of 400 to 450 nm was divided by the amount of each immobilized nOA-TA to obtain the fluorescence response performance value n_c . As shown in Figure 2-12b, the n_c value increased with smaller pore size, with the highest fluorescence response performance to $\cdot\text{OH}$ at 0.1 μm pore size. In the preparation of nOA-TA immobilized sheets, a methanol solution of nOA-TA was retained in the pores of a membrane filter and then dried to precipitate particulate nanocrystals of nOA-TA in the pores.^[10] Since the particle size of nOA-TA crystals precipitated in the pores was limited by the pore size, smaller pores resulted in smaller nOA-TA particles. The specific surface area of the nOA-TA particles increased as the particles became smaller. Therefore, the area of contact between nOA-TA and $\cdot\text{OH}$ generated by the low-pressure Hg lamp method also increased, which was thought to be responsible for the high fluorescence response performance.

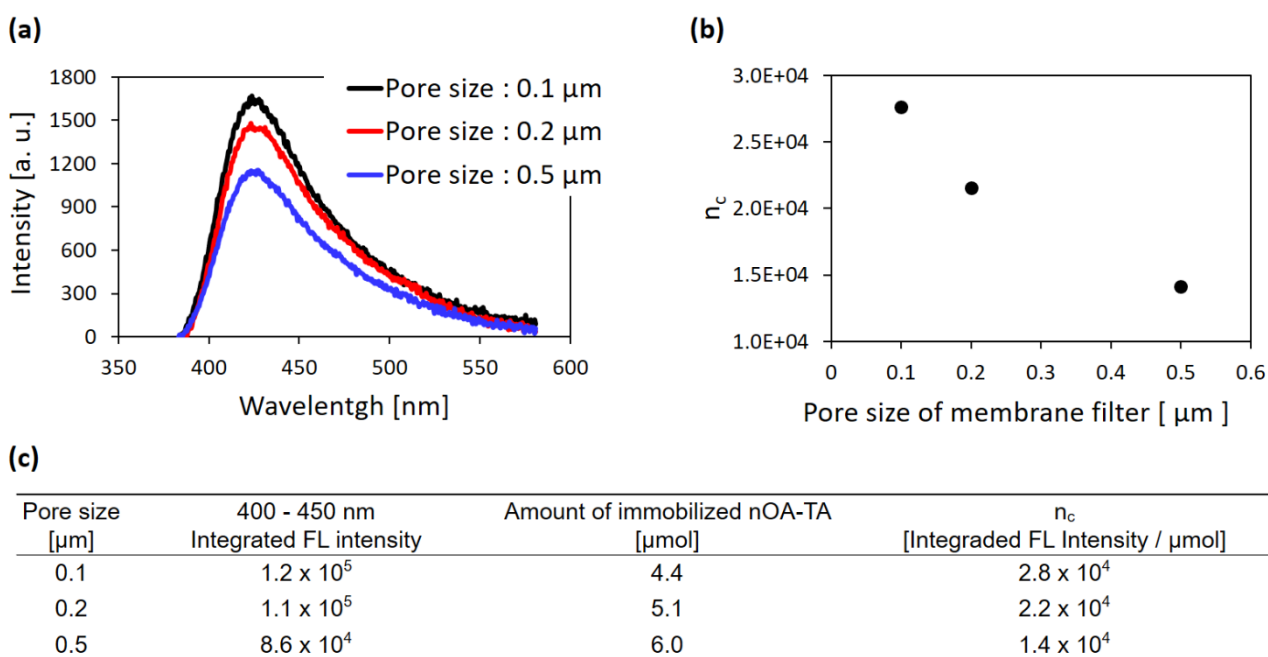


Figure 2-12. (a) Fluorescence spectra of methanol eluates of nOA-TA immobilized sheets prepared using membrane filters of different pore sizes and exposed to $\cdot\text{OH}$ for 2 h. (b) n_c versus pore size. (c) Table of integrated fluorescence (FL) intensity in the range of 400–450 nm, amount of nOA-TA immobilized on the sheets, and n_c .

It can be seen from the results in Figure 2-11 and Figure 2-12 that the use of nOA-TA with alkyl chain length of 8 and a membrane filter with a small pore size is effective in improving the fluorescence response performance to $\cdot\text{OH}$.

2.3.6 Procedure for deriving the HTA/TA ratio map from the fluorescent image of the nOA-TA immobilized sheet after $\cdot\text{OH}$ exposure

Figure 2-13 shows fluorescence images of the nOA-TA immobilized sheet (membrane filter pore size: $0.1\ \mu\text{m}$) before and after exposure to $\cdot\text{OH}$ for 2 hours using the low-pressure Hg lamp method. Fluorescence intensity increased after $\cdot\text{OH}$ exposure, which was attributed to the formation of fluorescent HTA by $\cdot\text{OH}$ exposure.^[10]

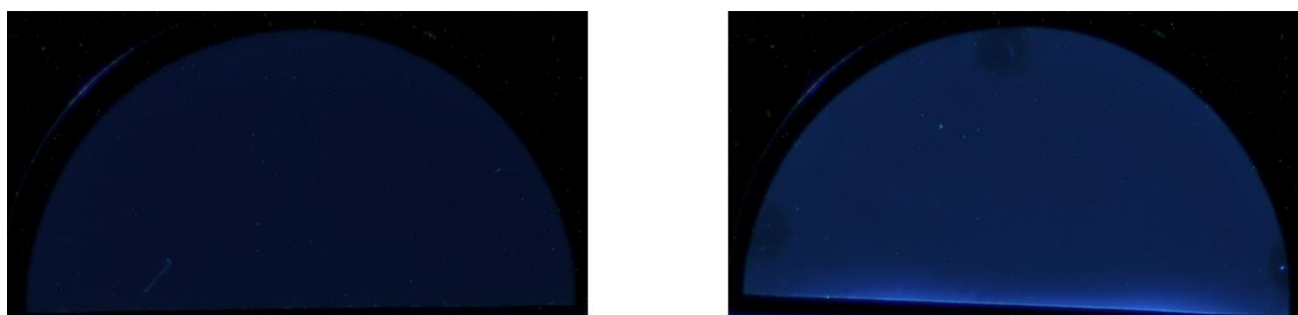


Figure 2-13. Fluorescence images before (left) and after (right) 2 h exposure to $\cdot\text{OH}$ generated by the low-pressure Hg lamp method. Excitation wavelength was 313 nm.

The procedure for converting the fluorescence image of the sheet after this $\cdot\text{OH}$ exposure into the HTA/TA ratio map is illustrated in Figure 2-14. First, fluorescence images of nOA-TA immobilized sheets with trace amounts of nOA-HTA were acquired. The sheet area on the fluorescence images was selected using image editing software (GIMP ver. 2.8), and the average blue pixel value (0-255) in the selected area was derived and plotted against the HTA/TA ratio. Next, this plot was linearly approximated to obtain the correlation equation between the HTA/TA ratio and the average blue pixel value. The fluorescence image of the sheet after $\cdot\text{OH}$ exposure (Figure 2-13, right) was then converted to the blue pixel map, and finally the HTA/TA ratio map was obtained using the correlation equation derived above.

The HTA/TA ratio map in Figure 2-14 shows that the HTA/TA ratio was locally high around the chord of the semicircle, where approximately 0.04% of TA was converted to HTA. Since the intensity of the incident 185 nm VUV light was stronger near the sapphire window, $\cdot\text{OH}$ generated by decomposition of water molecules was locally distributed around the chord of the semicircle close to the sapphire window, and it is most likely that TA reacted with more $\cdot\text{OH}$ near the chord to form more HTA.

Thus, it was shown that the distribution of gaseous $\cdot\text{OH}$ can be quantitatively visualized as a two-dimensional HTA/TA ratio map by using the nOA-TA immobilized sheet.

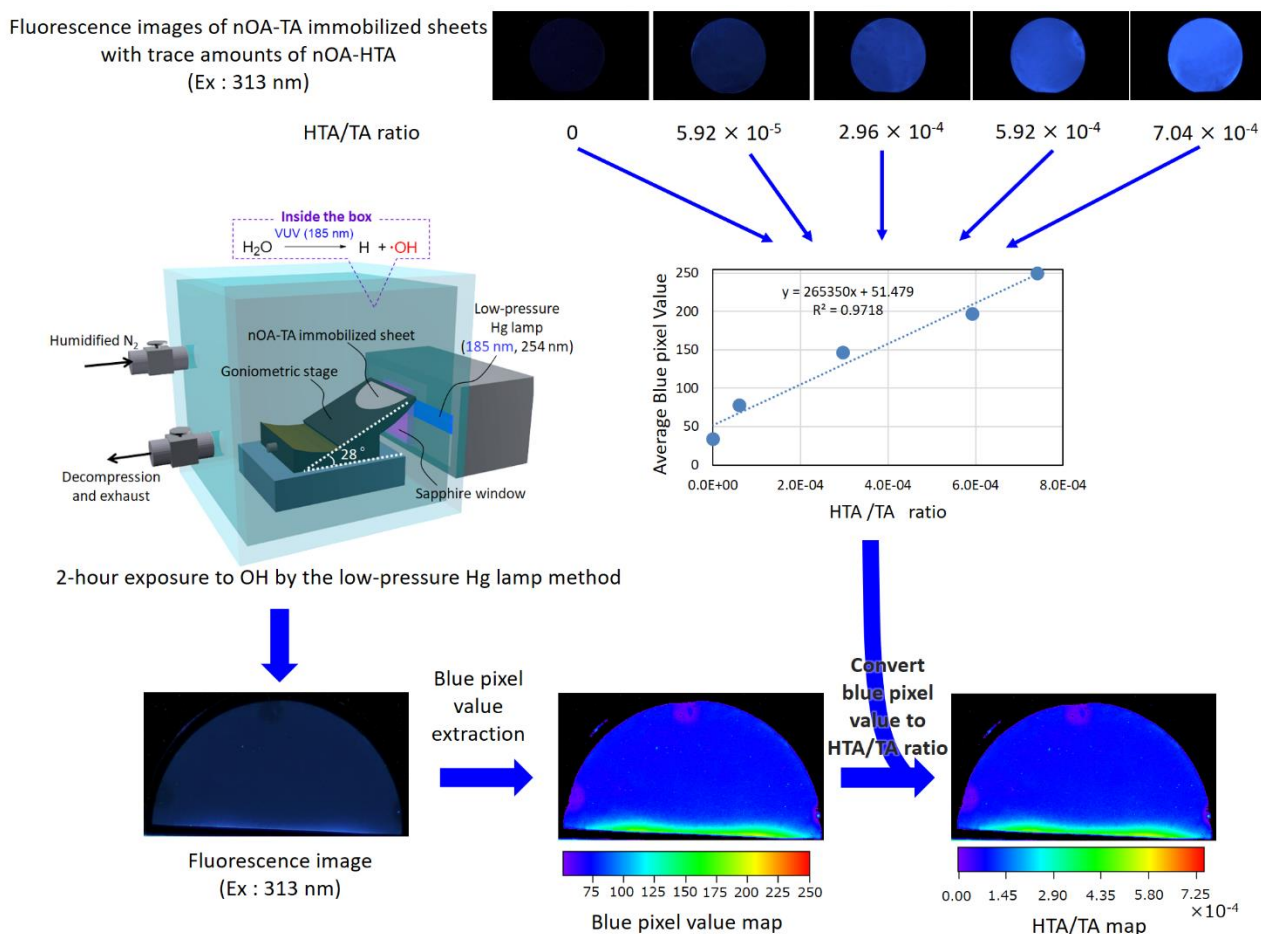


Figure 2-14. Procedure for converting the fluorescent image of the nOA-TA immobilized sheet to the HTA/TA ratio map.

2.4 Conclusion

The author has demonstrated that organic salts consisting of TPA and *n*-alkylamines with alkyl chains of 8 or more carbons can be immobilized on membrane filters by a simple dipping and drying process.

In the nOA-TA immobilized sheet, ESI-MS analysis revealed that a portion of TA in nOA-TA crystals reacted with $\cdot\text{OH}$ generated by the low-pressure Hg lamp method to form a trace amount of fluorescent HTA. This HTA formation exhibited a response with fluorescence emission at approximately 423 nm. An ideal response behavior was observed in which the fluorescence intensity increased with a longer $\cdot\text{OH}$ exposure time.

For nNA-TA and nDA-TA with alkyl chain lengths longer than 8, the fluorescence response performance was lower, likely due to stronger packing between long alkyl chains that restricted the

penetration of $\cdot\text{OH}$ into the crystal. Thus, the author confirmed that nOA-TA with an alkyl chain length of 8 exhibited the best fluorescence response performance to $\cdot\text{OH}$.

It was also found that the use of membrane filters with small pore size enhanced the fluorescence response performance. The smaller pore size increased the specific surface area of nOA-TA particles precipitated in the pores, resulting in a larger contact area between nOA-TA and $\cdot\text{OH}$.

Finally, the author established a procedure to convert fluorescence images of the nOA-TA immobilized sheet after $\cdot\text{OH}$ exposure into the HTA/TA ratio map, demonstrating that the distribution of gaseous $\cdot\text{OH}$ in space can be quantitatively visualized in two-dimensions.

Excellent portability of the nOA-TA immobilized sheet will enable anyone to easily measure the spatial distribution of gaseous $\cdot\text{OH}$ emitted from devices such as plasma systems and photocatalysts by simply placing the sheet at the desired $\cdot\text{OH}$ measurement position. Furthermore, the nOA-TA immobilized sheets can be prepared by a simple solution process, and the author believes that large-area and mass production of the sheets can be expected in the future by applying a roll-to-roll process.

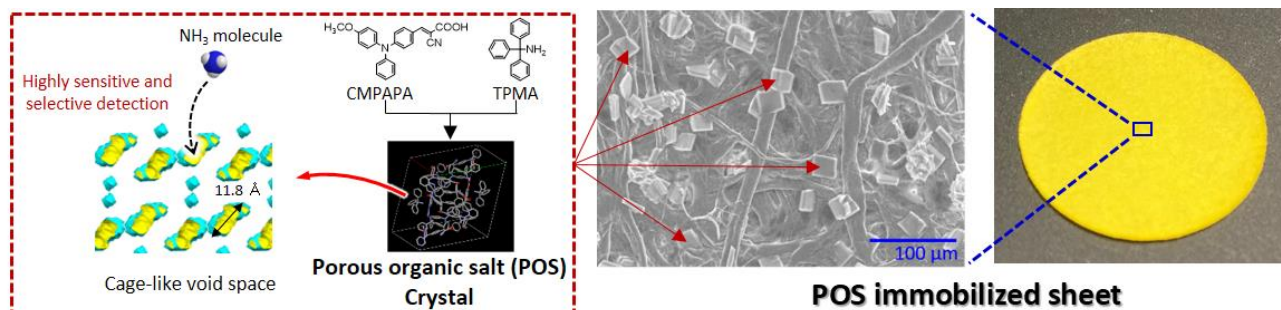
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Chapter 3

Fabrication of Porous Organic Salt-Immobilized Sheet by a Simple Solution Process and its Application to Gas Detection



Abstract: This chapter describes a porous organic material with higher processability than metal organic frameworks (MOFs) and covalent organic frameworks (COFs). A porous organic salt (POS) composed of 2-cyano-3(4-((4-methoxyphenyl)(phenyl)amino)phenyl) acrylic acid (CMPAPA) and triphenylmethylamine (TPMA) could be immobilized on a filter paper by a simple dipping and drying process. The author tested the applicability of the POS immobilized sheet as a gas sensor and found that the sheet exhibited a highly sensitive and selective fluorescence response to sub-ppm levels of ammonia.

3.1 Introduction

Porous organic materials have diverse topological structures, designable building blocks, and tunable pore sizes, which have been proposed for a wide variety of applications including storage, separation, purification, catalysis, and sensor.^[1] Typical examples are metal organic frameworks (MOFs),^[2] which utilize coordination bonds between organic molecules and metal atoms, and covalent organic frameworks (COFs),^[3] which utilize covalent bonds between organic molecules. However, MOFs and COFs are generally solvent insoluble powders, and the complexity of the post-process to immobilize them on a support substrate is a limitation to their practical use.

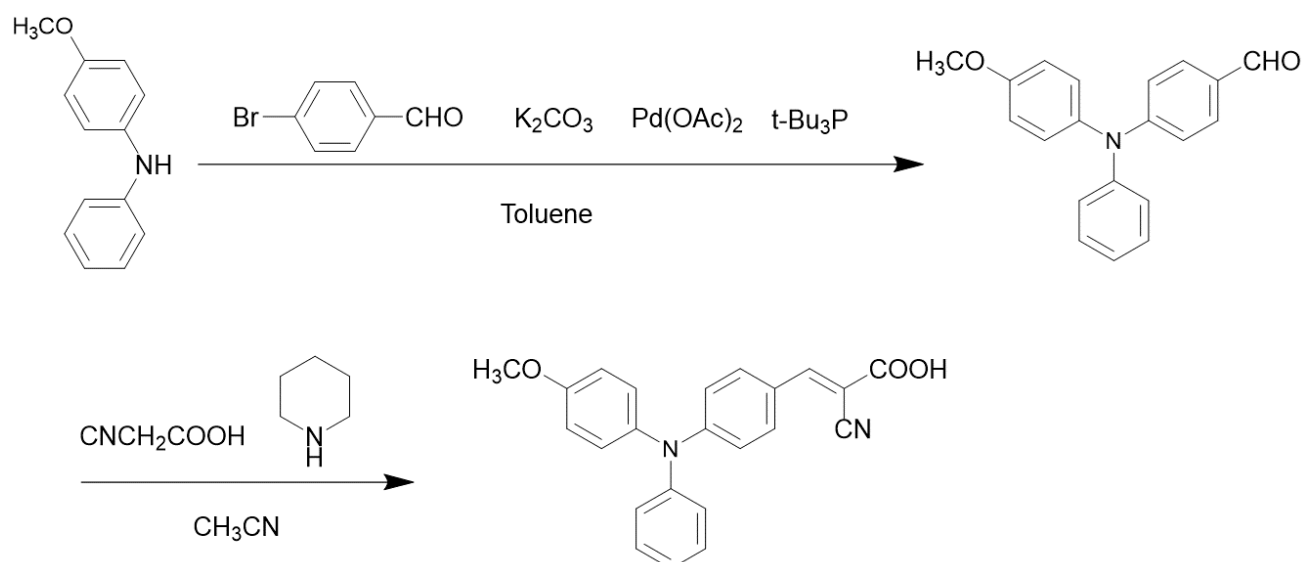
Tohnai and co-workers have previously reported the formation of [4+4] supramolecular clusters of aromatic sulfonic acid derivatives and triphenylmethanamine (TPMA) via charge-assisted hydrogen bonding, and the construction of porous structures through their various intermolecular interactions.^[4] These porous structures, called diamond-like porous organic salts (POSs), are known to exhibit guest-dependent fluorescence and selective gas adsorption.^[4b-d, 4f] However, the aforementioned studies have been limited to the handling of POSs in the form of single crystal or crystalline powder. POSs are so soluble in certain solvents that high processability by a simple solution process can be expected. Thus, the purpose of this paper is to present a practically superior porous organic salt (POS) which can be easily formed on a solid support, together with the evaluation test results of gas detection.

In this work, instead of using an aromatic sulfonic acid, a triphenylamine (TPA) derivative-based cyanoacrylic acid, 2-cyano-3-(4-((4-methoxyphenyl)(phenyl)amino)phenyl)acrylic acid (CMPAPA), was used. The carboxylic acid group forms an intermolecular hydrogen bond with the amine molecule to form a supramolecular host system.^[5] Given that TPA derivatives contain effective large π electron donating groups^[6] and exhibit multi-stimuli-responsive fluorescence,^[7] they are expected to display highly sensitive changes in fluorescence response on exposure to trace concentrations of chemicals. Herein, the author first prepared a POS consisting of CMPAPA and TPMA. In anticipation of practical applications, a sheet on which the POS crystals were immobilized, was described. Furthermore, the author investigated the fluorescence response to trace concentrations of chemical gases.

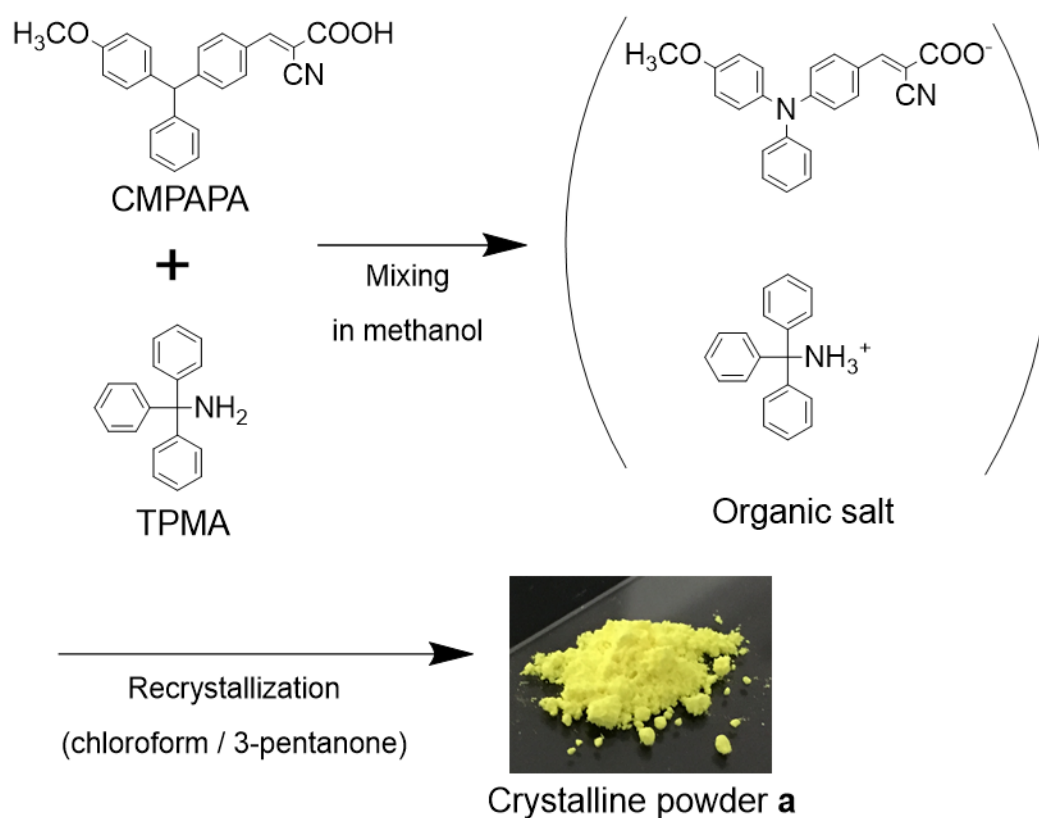
3.2 Experimental section

3.2.1 Preparation of crystalline powders and a single crystal composed of CMPAPA and TPMA

All chemicals and solvents were commercially available and used without any purification. CMPAPA was synthesized as shown in Scheme 3-1. CMPAPA and TPMA were mixed in methanol in a 1:1 molar ratio, and then methanol was removed under reduced pressure to form the organic salt. The organic salt was dissolved in a mixture of chloroform and 3-pentanone and slowly evaporated at room temperature to recrystallize giving yellow crystalline powder **a** (Scheme 3-2). The organic salt was dissolved in ethanol. Slow evaporation of the solvent at room temperature gave a single crystal.



Scheme 3-1. Synthetic route of CMPAPA.



Scheme 3-2. Chemical structure of organic salt and synthetic route of crystalline powder **a**.

3.2.2 Powder X-ray diffraction analysis

Powder X-ray diffraction (PXRD) patterns were measured by using a Rigaku Ultima IV with graphite-monochromatized Cu K α radiation ($\lambda = 1.54187 \text{ \AA}$) at room temperature.

3.2.3 Crystallographic analysis of single crystals

The X-ray diffraction data of the single crystal was collected on a two-dimensional X-ray detector (PILATUS 200 K/R) equipped with a Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu–K α radiation ($\lambda=1.54187 \text{ \AA}$) at 93 K. The cell refinements were performed with CrysAlisPro 1.171.39.5a software.^[8] The crystal structure was solved by direct method (SHELXT Version 2014/5).^[9] All calculations were performed with the observed reflections [$I > 2\sigma(I)$] with the CrystalStructure crystallographic software package,^[10] except for refinement which was performed by SHELXL.^[11] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. Deposition Numbers 2054899 contains the supplementary crystallographic data for this chapter.

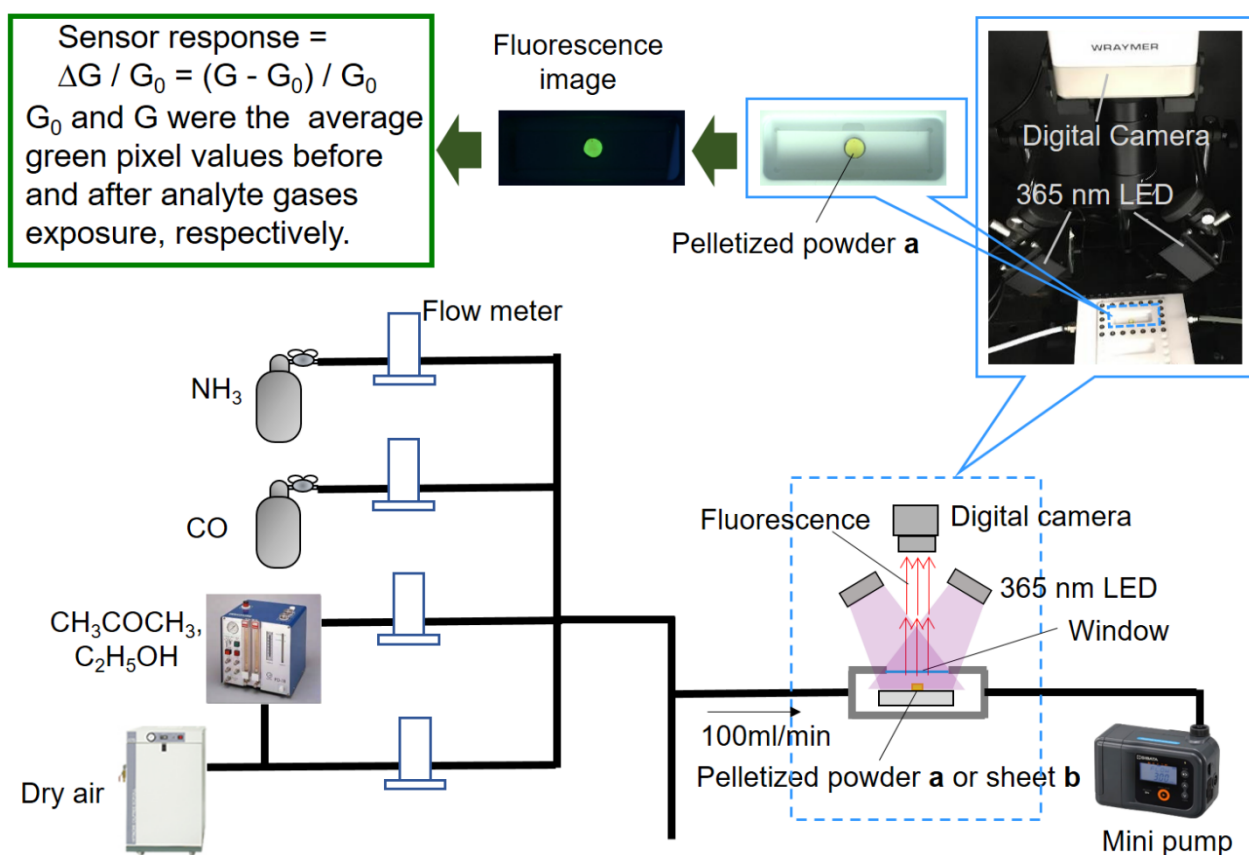
3.2.4 Scanning electron microscopy (SEM) measurements

SEM images were taken using a Hitachi High Tech SU3500 equipped with a high sensitivity low vacuum detector (Ultra Variable-Pressure Detector (UVD)) at an acceleration voltage of 15 kV (Low Vacuum Mode: 70 Pa).

3.2.5 Evaluation of response to chemical gases

Test samples were placed in a gas flow cell with a glass window, and yellow-green fluorescent images of the sample were acquired at 30 s intervals by irradiating UV light of wavelength 365 nm through the window while flowing various analyte gases which were diluted to predetermined concentrations with air or nitrogen. The average green pixel values (0-255) of the light-emitting area were extracted from the obtained fluorescent images and the sensor response was defined by $\Delta G/G_0 = (G - G_0)/G_0$, where G_0 and G are the average green pixel values before and after exposure to the analyte gases, respectively (Figure 3-1).

(a)



(b)

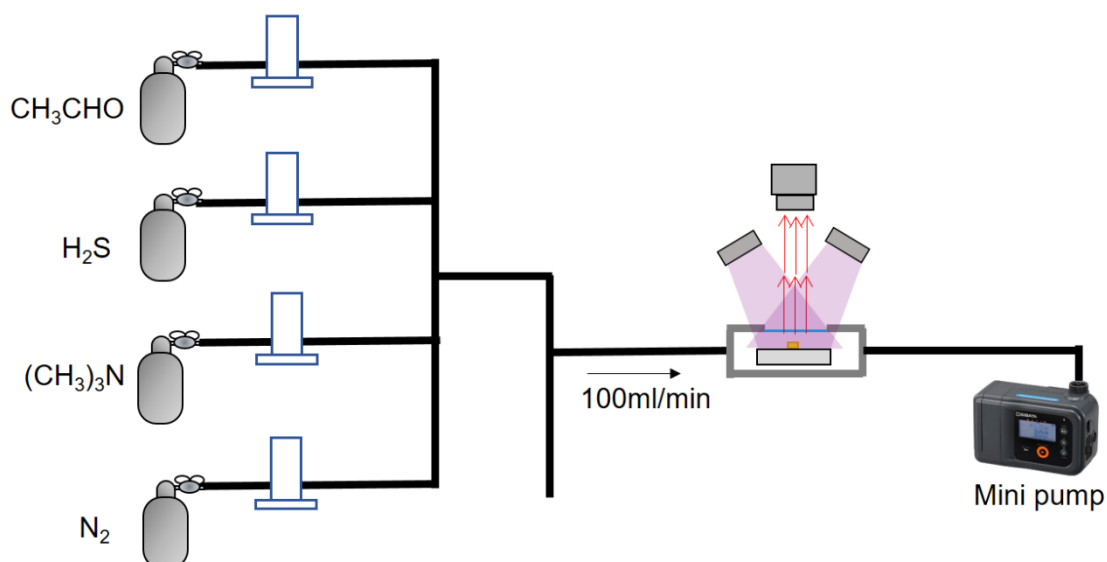


Figure 3-1. (a) Schematic diagram of an experimental system for measuring the fluorescence response to analyte gases diluted with dry air. (b) Schematic diagram of an experimental system for measuring the fluorescence response to analyte gases diluted with N₂.

3.3 Results and Discussion

3.3.1 Crystallographic analysis of an organic salt composed of CMPAPA and TPMA

The main peak of PXRD pattern of the powder **a** was in good agreement with that of the PXRD pattern predicted from the single crystal, indicating that the powder **a** and the single crystal had the same crystal structure (Figure 3-2). The single-crystal X-ray structural analysis revealed that POS was constructed as in the case of using aromatic sulfonic acid as the organic acid.^[4b, 4d, 4e] First, four CMPAPA and four TPMA molecules were connected via charge-assisted hydrogen bonds to form a tetrahedral supramolecular cluster as a building block (Figure 3-3a). Next, the bulky and awkward clusters were assembled by intermolecular interactions and then a higher-order structure with cage-like voids was constructed (Figure 3-3b and 3c). The cage-like void was caused by steric discomfort among the clusters.

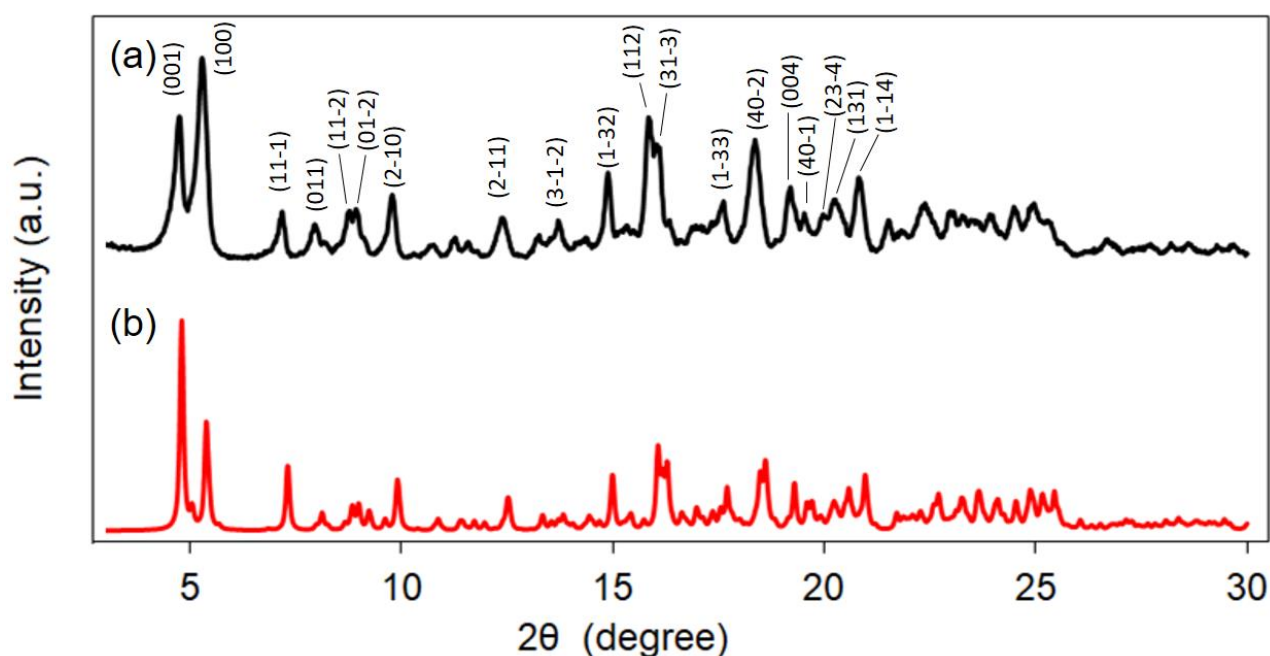


Figure 3-2. (a) PXRD pattern of the powder **a**. (b) PXRD pattern predicted from the single crystal.

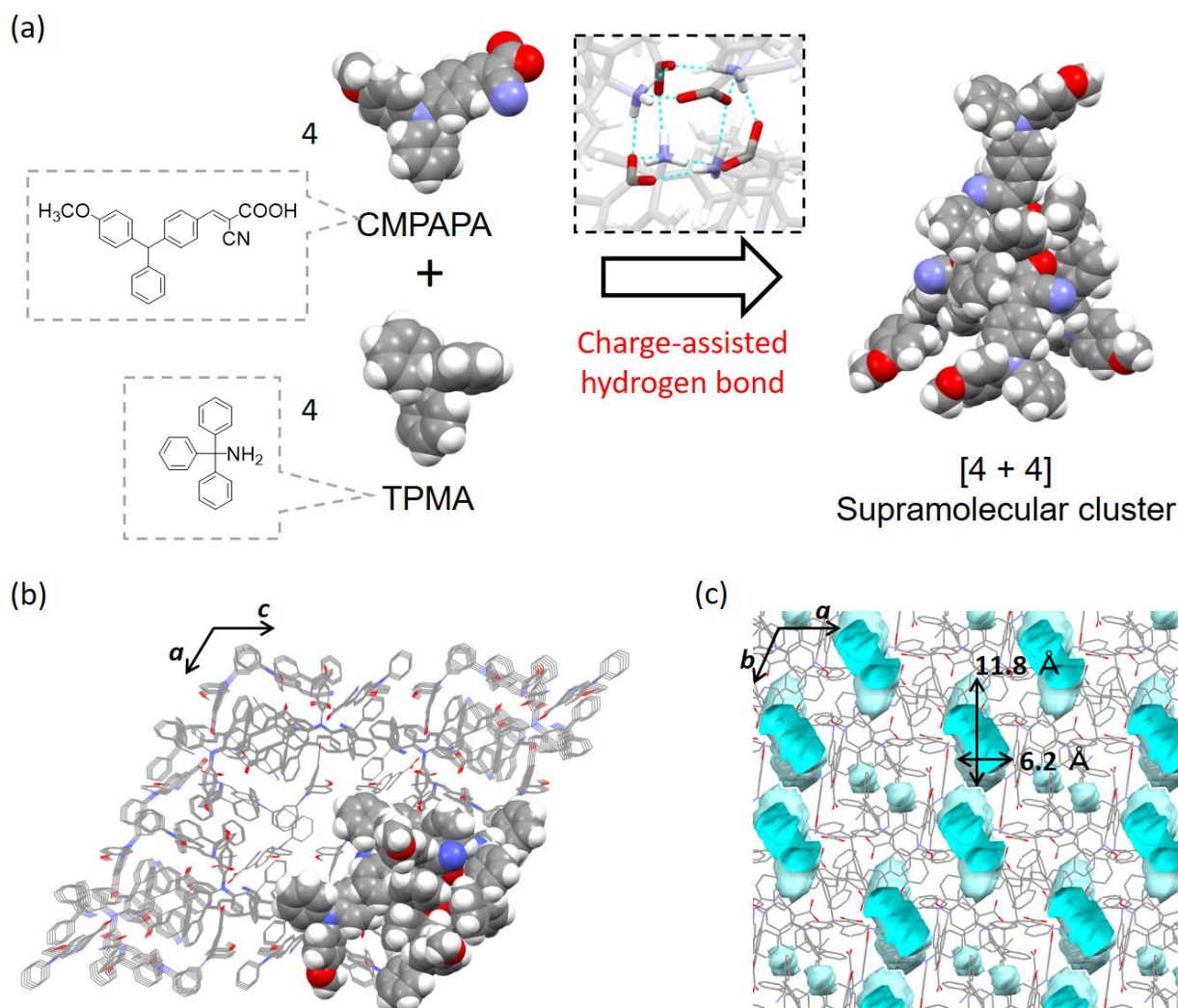


Figure 3-3. (a) Supramolecular cluster composed of CMPAPA and TPMA. (b) Crystal structure viewed along the *b*-axis. Ethanol molecules are omitted for clarity. Hydrogen atoms are omitted for clarity except in the space-filling model of the cluster. (c) Void space visualized by mercury with a probe radius of 1.2 Å and a grid spacing of 0.7 Å. Ethanol molecules and hydrogen atoms are omitted for clarity.

3.3.2 Preparation and evaluation of a POS immobilized sheet

In Chapters 1 and 2, the author demonstrated that particulate crystals of the organic salt consisting of terephthalic acid and *n*-alkylamine can be immobilized on a porous membrane filter.^[12] To demonstrate the high processability of the POS, experiments were conducted to immobilize the powder **a** in a wide area on a porous support (Figure 3-4a). The organic salt composed of CMPAPA and TPMA was dissolved in a mixed solvent of chloroform and 3-pentanone and adjusted to a concentration of 4.8×10^{-2} mol/L. A filter paper (KIRIYAMA, No. 4) was immersed in the solution such that the solution was retained in the pores of the filter paper. The immersed filter paper was removed from the solution, dried at room temperature for 24 hours, and subjected to SEM and PXRD. The low-vacuum SEM

image indicated that particulate solids with grain sizes around 10–30 μm were immobilized between the fibers of the filter paper (Figure 3-4b). Furthermore, well-defined light emission was observed from these particulate solids in the cathodoluminescence image (Figure 3-4c). Also, the main peak of the PXRD pattern of the filter paper after immersion and drying was in good agreement with that of the powder **a** (Figure 3-4d). That is, the author succeeded in producing POS immobilized sheet **b**, on which luminescent microcrystals with the same structure as the powder **a** were immobilized.

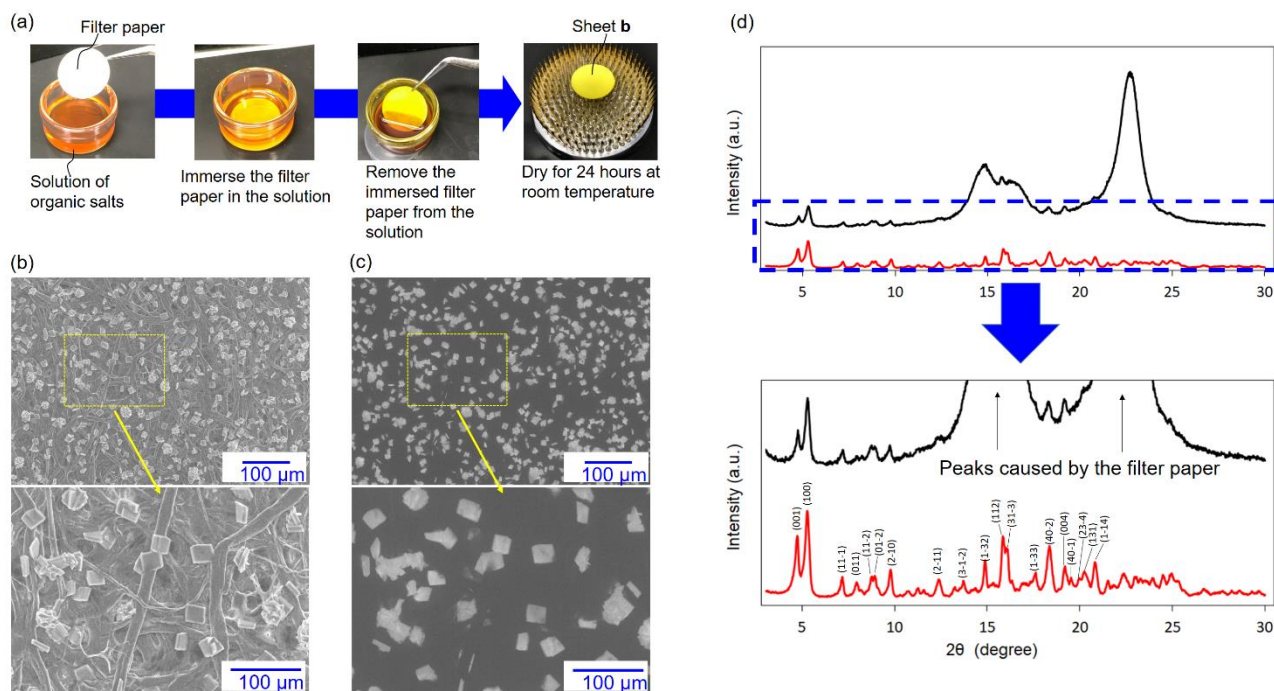


Figure 3-4. (a) Procedure for forming the powder **a** on a filter paper by a simple solution process. (b) Low-Vacuum SEM images of the filter paper after immersion and drying (UVD: Bias ON). (c) Cathodoluminescence images of the filter paper after immersion and drying (UVD: Bias OFF). (d) PXRD patterns of the filter paper after immersion and drying (black line) and PXRD patterns of the powder **a** (red line).

3.3.3 Response tests to chemical gases

The responses of the powder **a** and the sheet **b** to chemical gases were evaluated using the experimental system shown in Figure 3-1. Figure 3-5 shows the sensor response of the pelletized powder **a** when gaseous ammonia (NH_3) at sub-ppm concentration was flowed. $\Delta G/G_0$ increased during the introduction of NH_3 (30–60 min) and decreased gradually after the flow of NH_3 was stopped (60–90 min). The $\Delta G/G_0$ values showed a concentration-dependent change and, even for a low concentration of 50 ppb, a well-defined response was observed. The fluorescence spectra of the powder **a** before and after the introduction of 1000 ppb NH_3 for 30 minutes are shown in Figure 3-6. The intensity of the fluorescence spectrum with an emission maximum at about 525 nm increased after NH_3 introduction, which corresponded to an increase in $\Delta G/G_0$ caused by the introduction of NH_3 as observed in Figure 3-6b. Five repeated $\Delta G/G_0$ responses for 1000 ppb NH_3 were almost identical, and thus confirming

that the powder **a** could detect NH_3 with high repeatability (Figure 3-7). From the results above, it appears that the increase in $\Delta G/G_0$ by the introduction of NH_3 is attributed to the adsorption of NH_3 molecules onto the powder **a**, and the decrease in $\Delta G/G_0$ from the cessation of NH_3 flow reflects the desorption of NH_3 molecules from the powder **a**. The responses to analyte gases other than NH_3 (trimethylamine, hydrogen sulfide, ethanol, acetone, acetaldehyde, and carbon monoxide) are shown in Figure 3-8. Surprisingly, no clear increase in $\Delta G/G_0$ was observed for analyte gases other than NH_3 . These results indicated that NH_3 was sensed by the powder **a** with high selectivity. Presumably, the cage-like voids in the crystals act as a "molecular sieve," and NH_3 molecules, which are smaller than other analytes such as trimethylamine, are selectively taken up and physically adsorbed, and N atom on TPA moiety of CMPAPA, which is highly electronegative, accepts the hydrogen (positive charge) of NH_3 , resulting in a change in CMPAPA quantum yield and modulation of fluorescence intensity.

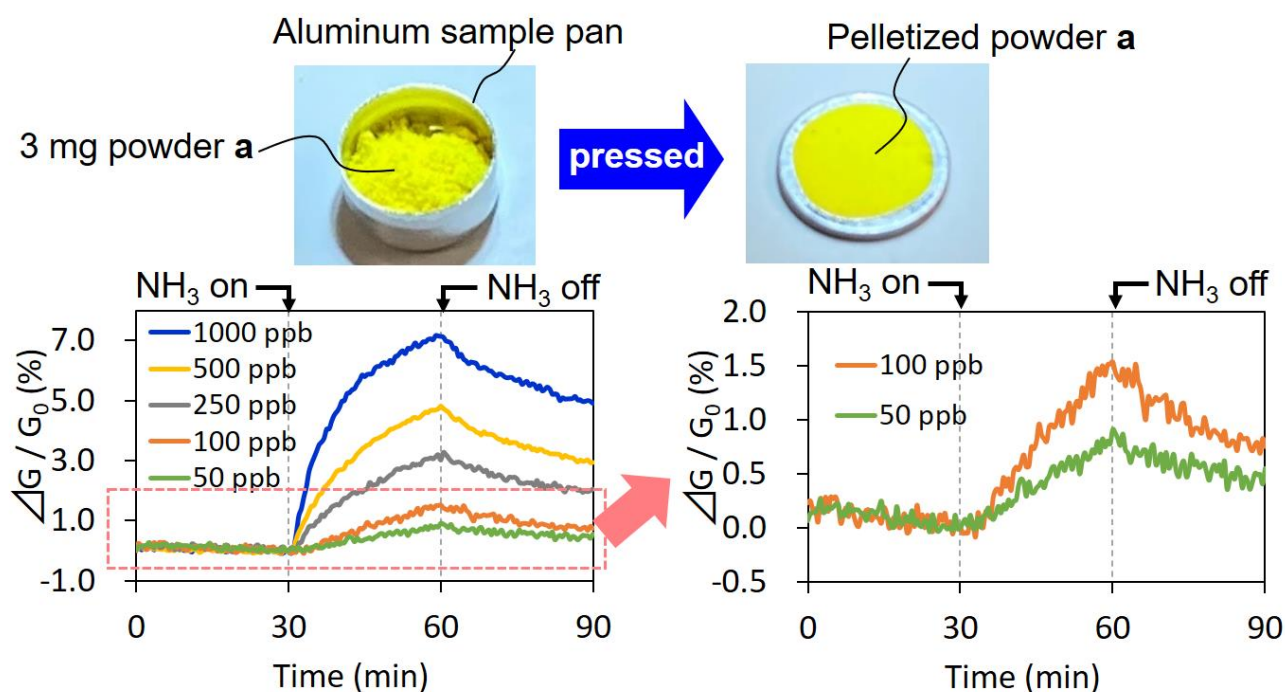


Figure 3-5. Fluorescence responsiveness of the pelletized powder **a** to sub-ppm NH_3 .

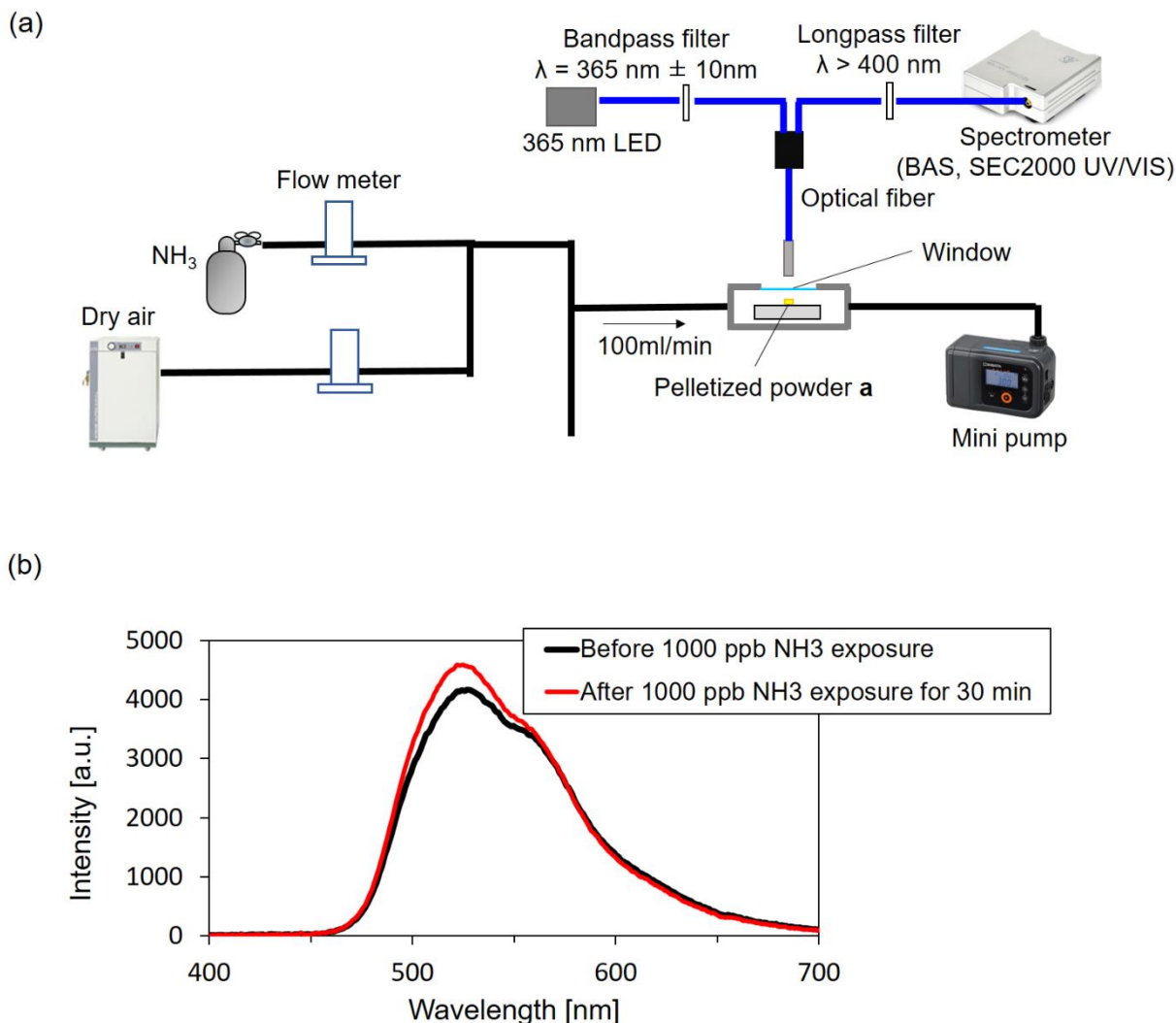


Figure 3-6. (a) Schematic diagram of an experimental system for measuring fluorescence spectra while exposing NH_3 to the pelletized powder **a**. (b) Fluorescence spectra of the pelletized powder **a** before and after exposure to 1000 ppb NH_3 .

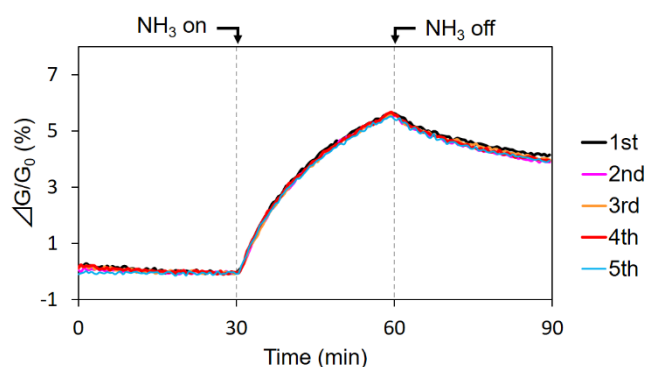


Figure 3-7. Results of five repeat measurements of the fluorescence response to 1000 ppb NH_3 using a single pelletized powder **a**. After each measurement, the powder **a** was exposed to dry air flowing at 100 ml/min for 12 hours before the next measurement was performed.

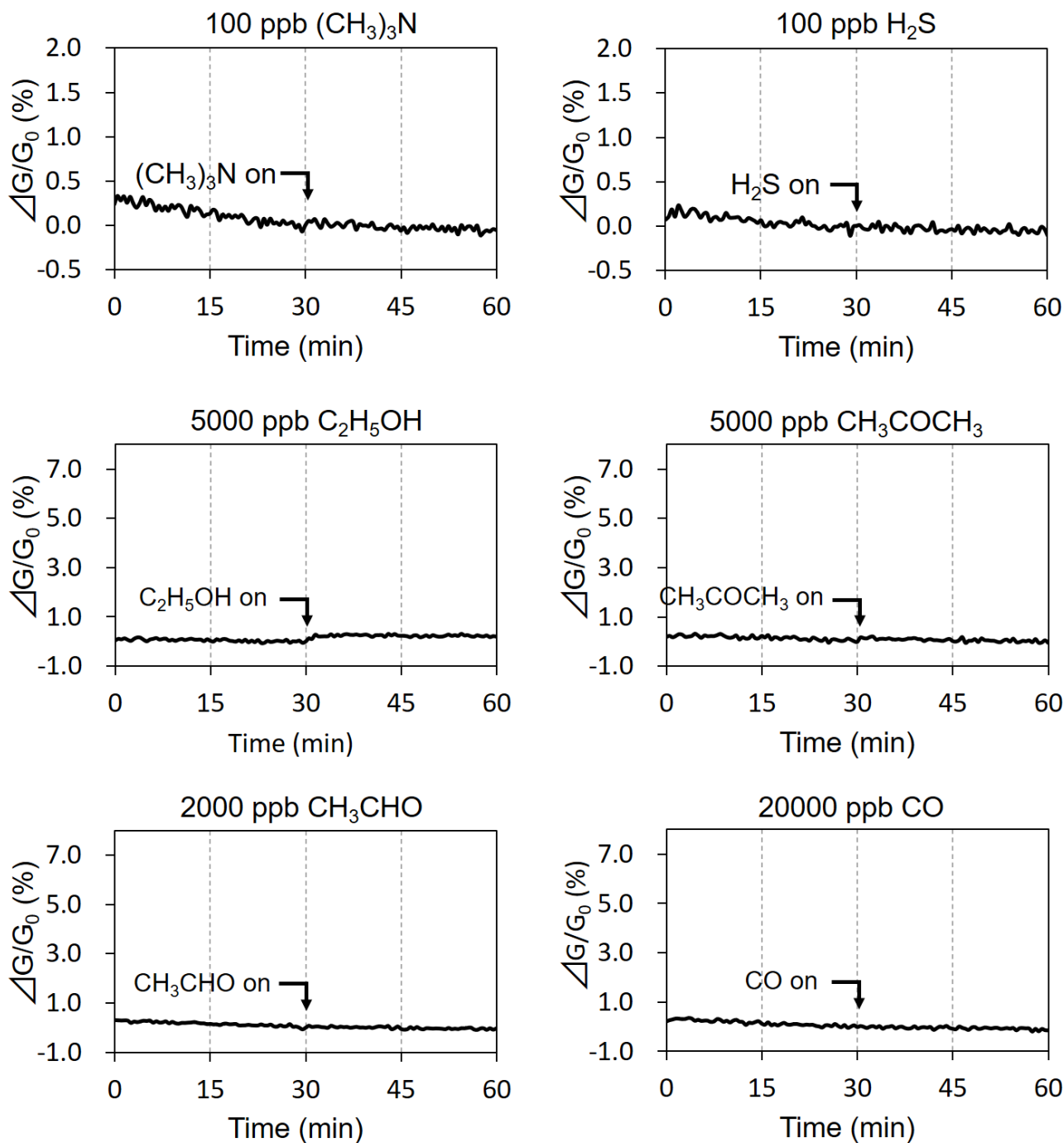


Figure 3-8. Fluorescence responsiveness of the pelletized powder **a** to 100 ppb trimethylamine ((CH₃)₃N), 100 ppb hydrogen sulfide (H₂S), 5000 ppb ethanol (C₂H₅OH), 5000 ppb acetone (CH₃COCH₃), 2000 ppb acetaldehyde (CH₃CHO), and 20000 ppb carbon monoxide (CO).

Figure 3-9 shows the $\Delta G/G_0$ responses of the sheet **b** to diluted NH₃. Clear increases in $\Delta G/G_0$ on sub-ppm NH₃ exposure were observed as was the case for the powder **a**. That is, a highly sensitive NH₃ sensor sheet was realized through a simple solution process at normal temperature and pressure. This

approach of simultaneous precipitation and immobilization of organic salt crystals on a porous support is expected to significantly improve ease of operation and greatly expand the scope for NH_3 sensing from the viewpoints of enhanced stability against physical stimuli such as contact, being able to cut and fabricate the sensor sheet into desired sizes and shapes appropriate to intended use, and being able to evaluate the spatial distribution of NH_3 .

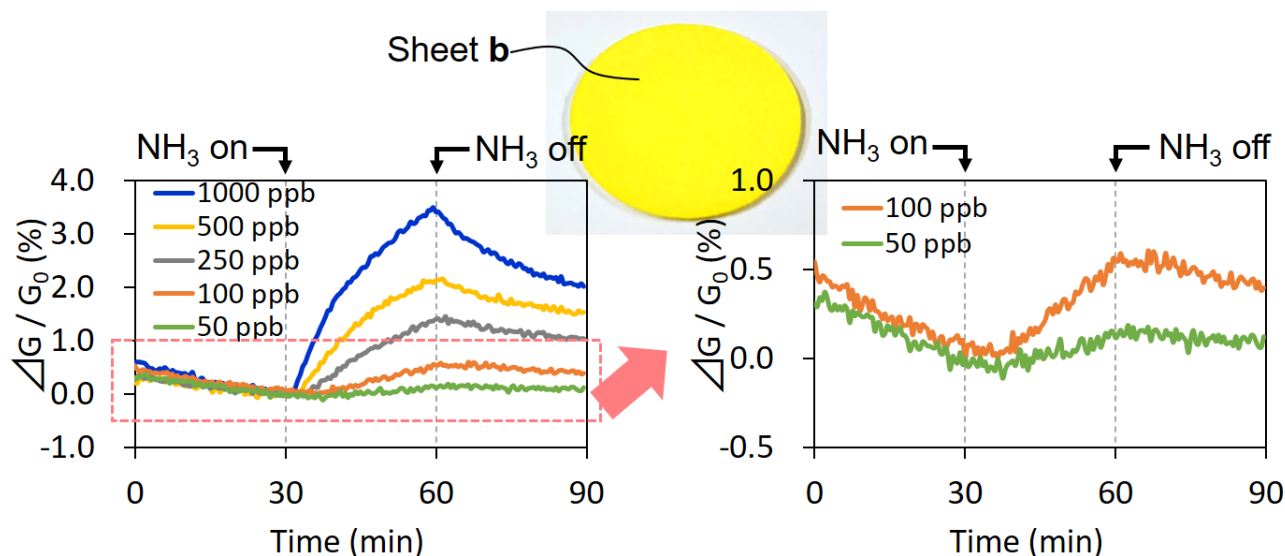


Figure 3-9. Fluorescence responsiveness of the sheet **b** to sub-ppm NH_3 .

3.4 Conclusion

An organic salt composed of CMPAPA and TPMA provides a porous crystal with cage-like void space. The POS crystals can be formed on a filter paper uniformly by a simple dipping and drying process and this POS immobilized sheet displays highly sensitive fluorescence responses to sub-ppm levels of ammonia. Thus, the POS is an excellent organic porous material from a practical standpoint in that it has high processability with a simple solution process at room temperature and normal pressure. In the future, mass production of the POS immobilized sheet can be expected by applying a large scale roll-to-roll process.

3.5 References

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Summary

This thesis has described novel and practical gas sensing materials based on organic salt crystals, which have higher processability than conventional porous materials such as metal organic frameworks (MOFs) and covalent organic frameworks (COFs). The author successfully constructed organic salts with void structures that enable highly sensitive and selective detection of target gases, and further demonstrated the concept of fabricating large-area gas sensor sheets by taking advantage of high solubility of the organic salts in certain solvents.

Chapter 1 describes a newly developed solid gaseous OH radical ($\cdot\text{OH}$) indicator. *n*-Alkylammonium terephthalate with an alkyl chain length greater than 8 had a crystal structure in which the alkyl chains were arranged parallel to each other and the zero-dimensional voids were adjacent to the terephthalate (TA). These parallel alkyl chains acted as hydrophobic blocks. Due to the presence of the voids, $\cdot\text{OH}$ penetrated into the bis(*n*-octylammonium) terephthalate (nOA-TA) crystals and reacted with TA to form fluorescent hydroxyterephthalate (HTA), allowing $\cdot\text{OH}$ to be detected. In addition, nOA-TA nanocrystals were successfully immobilized uniformly on a membrane filter, allowing the spatial distribution of gaseous $\cdot\text{OH}$ to be visualized.

Chapter 2 describes the results of a more detailed validation of the $\cdot\text{OH}$ detection principle and the fluorescence response performance for the practical application of the gaseous $\cdot\text{OH}$ measurement method mentioned in Chapter 1. Using high-sensitivity mass spectrometry, the author demonstrated that when the nOA-TA immobilized sheet is exposed to gaseous $\cdot\text{OH}$, some of the TA reacts with $\cdot\text{OH}$ to form trace amounts of HTA. It was also found that the fluorescence response performance was improved by using nOA-TA with an alkyl chain length of 8 and a membrane filter with a smaller pore size. In addition, a procedure was established to convert a fluorescence image of the nOA-TA immobilized sheet after $\cdot\text{OH}$ exposure into an HTA/TA ratio map and demonstrated that the spatial distribution of gaseous $\cdot\text{OH}$ can be quantitatively visualized. The author believes that the excellent portability of the nOA-TA immobilized sheet will enable easy on-site measurements of gaseous $\cdot\text{OH}$ emitted from plasma devices, photocatalysts, and other equipment.

Chapter 3 describes a porous organic salt (POS) capable of detecting ammonia (NH_3). An organic salt composed of 2-cyano-3(4-((4-methoxyphenyl)(phenyl)amino)phenyl) acrylic acid (CMPAPA) and triphenylmethylamine (TPMA) gave a porous crystal with cage-like void space. The porous organic salt (POS) crystal powder physically adsorbed sub-ppm NH_3 and exhibited a response with changes in fluorescence intensity. The POS microcrystals were successfully precipitated and immobilized on a filter paper, a porous support with macropores, by a simple dipping and drying process, as well as *n*-alkylammonium terephthalate described in Chapters 1 and 2. This POS immobilized sheet, like the crystal powder, exhibited highly sensitive fluorescence responses to sub-ppm levels of NH_3 .

These studies have shown that the organic salt crystals not only have high designability such that they exhibit excellent selective response to target gases with the appropriate combination of organic acid and amine molecules, but also have high processability with solubility in certain solvents, making it possible to fabricate large-area sensor sheets using a very simple solution process. The latter feature is particularly noteworthy from the point of view that it has been difficult to fabricate large-area films with conventional porous materials (MOFs and COFs), which have poor processability. In the future, it is expected that gas sensor sheets using organic salts will be mass-produced by the roll-to-roll process and developed into practical gas sensors that can be used in various applications, such as operation control of gas-emitting devices, indoor air quality control, health diagnosis by biological gases, and food freshness monitoring.

Finally, the configuration, principles, and characteristics of the gas detection methods presented in this thesis are summarized in Table S-1. The $\cdot\text{OH}$ measurement described in Chapters 1 and 2 is for single use because the formation of HTA by the reaction of TA with $\cdot\text{OH}$ is irreversible. On the other hand, the NH_3 measurement described in Chapter 3 can be performed repeatedly because the adsorption and desorption of NH_3 on the POS is reversible. Both measurements require an ultraviolet (UV) light source to excite the organic salts and a digital camera to detect the fluorescence. Recent technological advances have made both the light source and the camera increasingly sophisticated and compact. It is therefore quite feasible to make the entire sensor system significantly miniaturized and portable by using, for example, a compact UV LED and a high-sensitivity camera of a high-end smartphone.

Table S-1. Configuration, detection principle, and characteristics of the gas sensors in this paper.

Chapter	Target gas	Gas sensing material	Transducer	Gas Detection principle	Repeatability	Possibility of system miniaturization
1 and 2	$\cdot\text{OH}$	n-Alkylammonium terephthalate immobilized sheet	RGB digital camera	Detection of fluorescence from HTA formed by the reaction of TA with OH	No (Disposable use)	Yes (Use of compact LED light sources and high sensitive smartphone cameras)
3	NH_3	POS (composed of CMPAPA and TPMA) immobilized sheet	RGB digital camera	Detection of changes in fluorescence intensity due to adsorption of NH_3	Yes	

List of Publications

- (1) Primary Ammonium Terephthalate Salts with High Moisture Resistance and Their Use in the Detection of OH Radicals.
Teppei Hosokawa, Sachiko Inazato, and Norimitsu Tohnai
ChemPlusChem **2020**, 85, 2666.
- (2) Fabrication of Porous Organic Salt-immobilized Sheet by a Simple Solution Process and its Application to Gas Detection.
Teppei Hosokawa, Sachiko Inazato, Atsushi Yamamoto, and Norimitsu Tohnai
Mater. Lett. **2022**, 327, 133054.
- (3) Development of *n*-Alkylammonium Terephthalate Immobilized Sheet for Facile Measurement of Spatial Distribution of Gaseous OH radical (OH).
Teppei Hosokawa, and Norimitsu Tohnai
Jpn. J. Appl. Phys. **2023**, 62, 107001.

Related Patents

- (1) Complex Crystal and Chemosensor Provided with Same.
Teppei Hosokawa, Norimitsu Tohnai, and Mikihiko Nishitani
United State Patent, US 11434213 B2, 2022
- (2) Organic salt, Hydroxy-Radical Sensor Including Same, and Detection Medium.
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