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Ionic liquids tailored for reaction-based gas sensing on quartz crystal microbalance

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Abstract: Gas sensing technologies are of importance for a variety of industrial, environmental, medical, and even military applications. Many gases, such as man-made or naturally occurring volatile organic compounds (VOCs), can adversely affect human health or cause harm to the environment. Recent advances in "designer solvents" and sensor technologies have facilitated the development of ultrasensitive gas sensing ionic liquids (SILs) based on quartz crystal microbalance (QCM) that can real-time detect and discriminate VOCs. Based on specific chemical reactions at room temperature, thin-coated functionalized ionic liquids on quartz chips are able to capture VOCs chemoselectively with a single-digit parts-per-billion detection limit. The amalgamation of tailor-made functional SILs and QCM results in a new class of qualitative and semiquantitative gas sensing device, which represents a prototype of electronic nose. This review vignettes some conventional gas sensing approaches and collates latest research results in the exploration of SIL-on-QCM chips and gives an account of the state-of-the-art gas sensing technology.

Keywords: chemoselective gas sensing; ionic liquid; label-free detection; quartz crystal microbalance; volatile organic compound.

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Introduction

Gas is one of the four fundamental states of matter that is considered as being between the liquid and plasma states. A pure gas can be composed of single atoms (e.g. noble gas), one type of atom (e.g. oxygen) or organic molecules made from a variety of atoms (e.g. acetone). On the contrary, a gas mixture contains a variety of pure gases that are very common such as the air that we are breathing in at the moment regardless of various trace amounts of harmful gases that might come with it. Unlike other states of matter, what distinguishes gas from liquid and solid is the distinct separation of the individual gas molecules, which makes them moving fast and freely, and is invisible to the human naked eyes. In addition, the interaction of gas molecules in the electric and gravitational fields is considered negligible. So, how do we know the existence of this intangible matter before devastating consequences to happen? The importance of olfactory systems among higher eukaryotes is revealed by the significant proportion (as much as 4%) of the genomes that is devoted to encoding the proteins of smell (Firestein 2001). In the human olfactory system, gas is inhaled into nasal cavity and then diffuses through mucus to olfactory epithelium receptor cells. The peripheral system senses the external stimulus and then the central system encodes it as an electric signal in neurons, whereby all signals are integrated and processed in the central nervous system. The mechanisms of a gas sensing device are similar to human olfaction, in which it is typically composed of two essential components, i.e. a sensing material or a receptor and a transducer or an electronic processor. An array of gas sensors can simulate the mammalian olfactory system that senses a myriad of aromas. The gaseous molecules are collected by sampling methods such as a bubbler, diffusion methods, headspace sampling, or pre-concentrators. The gas sample passes through the sensor array and induces physical or chemical changes on the sensor chip, which are transduced into electrical signals or patterns and then processed by a computer system. Figure 1 illustrates the comparison of the mammalian olfactory system and a quartz crystal microbalance (QCM) gas sensing system as an example. The sensing material should be able to

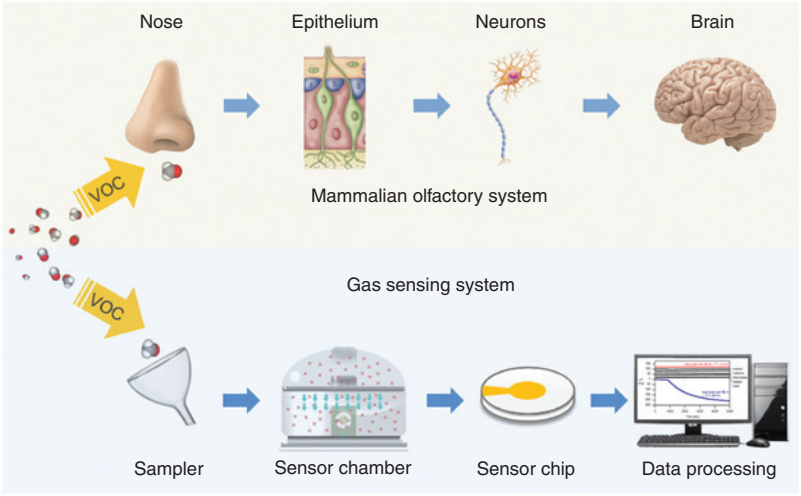


Figure 1: Schematic comparison of mammalian olfactory system and the QCM gas sensing system.

capture or recognize the presence of the analyte(s), while the transducer transforms the recognition process to a read-out or a physical signal such as electric current, electric potential or optical intensity. A gas sensing material can be perceived as the peripheral system in the human olfactory system, which serves as the receptor or first line of molecular recognition prior to signal transduction and processing at the transducer or electronic processors. This review is intended to give a brief introduction of current gas sensing technologies and latest advances in the field of gas sensing ionic liquids (SILs) based on QCM, which include their sensing principles, applications, limitations, and future directions.

A gas sensor detects a certain type of gas and measures its concentration in the vicinity. Like all other sensors, a gas sensor requires a device or a transducer to interact with a gas that senses changes or input in quantities and generates corresponding output or signal. Similar to choosing fragrances at the counter, some are pleased by floral or citrus scent, while others scrunch up noses when merely smell a whiff of woody or chypre note. Mimicking the biological olfactory system, an array of gas sensors should be able to selectively distinguish gases and faithfully converts input of environs into a readable signal, which will help the user to make judgments or decisions, depending on the purpose of detection. It may be simply about the personal preference of taste or a serious matter of life and death. The applications of gas sensing technology cover a wide range of areas that include, but are not limited to, (1) environmental protection (e.g. greenhouse gases and automobile emissions), (2) manufacturing industry (e.g. combustible, flammable and toxic gases), (3) disease diagnosis [e.g. volatile organic compounds (VOCs)], (4) indoor air quality monitoring (e.g. asphyxiant and hazardous gases), and (5) homeland security and the military (e.g. biological and chemical warfare agents).

With no doubt, there is an ever increasing demand for reliable gas sensors with the progression of human civilization. For example, air pollution has been a major health threat and an international issue since the launch of the Industrial Revolution. The U.S. Environmental Protection Agency tracks air pollutants such as carbon monoxide, nitrogen oxides and sulfur dioxide that are associated with adverse effects on human health. On the contrary, the analysis of volatile compounds or odor measurements by gas sensors has been widely used in the areas of food processing (e.g. grading of agro-products such as coffee and spices; Wu et al. 2014) and disease diagnosis (e.g. VOCs in exhaled breath of cancer or diabetes patients; Konvalina and Haick 2014, Tung et al. 2014). Interestingly, dogs have been used by law enforcement personnel to detect or track explosives, narcotics and cancers through their sensitive noses (Quignon et al. 2012, Taverna et al. 2015). Compared with human, a dog's olfactory epithelium not only has greater surface area (170 vs. 100 cm^2) but also more densely innervated (about 100 times more receptors/cm^2). By reproducing mammalian olfaction using sensor arrays and pattern recognition systems, electronic noses have been also developed to detect a variety of gases and generate odor profile or fingerprint for statistical analysis (Röck et al. 2008). In addition, a variety of nanomaterials have been used for VOC sensing, such as field effect transistors (FETs) based on single-walled carbon nanotubes (CNTs; Kuang et al. 2010) and nanowires of various materials (Paska et al. 2011). These gas sensing systems require a set of active materials that interact with volatile compounds and transduce the chemical vapors into electrical signals. Conventional gas sensing methods can be

generally categorized into (1) conductivity sensors (e.g. metal-oxide semiconductors and conducting organic polymers), (2) piezoelectric sensors [e.g. QCM and surface acoustic waves (SAW)], and (3) spectroscopic instruments. Each gas sensing technology can be used solely or multiple sensing methods can be also employed to devise an electronic nose of particular interests. In addition, other directions of gas sensing have been investigated such as gas chromatography (GC) and mass spectrometry (MS).

Nanomaterials such as FETs based on single-walled CNTs (specific recognition) and nanowires of various materials (semiselective recognition) are frequently used as highly sensitive transduction elements. For nanomaterials in the application of disease detection, please refer to the aforementioned article (Konvalina and Haick 2014). Conventional gas sensors use a "lock-and-key" design result in transducers that have high sensitivity [detection limits down to parts per billion (ppb)] and selectivity. However, it is not particularly practical for the analysis of complex analytes due to the fact that most sensors exhibit some cross-reactivity to structurally similar compounds. This is where cross-reactive sensors (an array of semiselective sensing materials) come into play to achieve higher flexibility by applying pattern recognition and classification algorithms (Tisch and Haick 2010). Such systems are referred to as electronic noses due to their resemblance to the mammalian olfactory system. Nevertheless, higher selectivity comes at the price of irreversibility, lengthy recovery times, memory effects, and lower sensitivity (detection limits down to 100 ppb). No single method can meet all the requirements at the moment but might be complementary to one another.

Our laboratory has a long-standing interest in QCM and ionic liquids; thus, we focus on the development of chemoselective SIL-based QCM gas analysis system for the detection of VOCs. Many man-made VOCs are excellent markers for a variety of problems that come with human civilization regardless they are also the culprits or results of environmental pollutions and modern diseases (Nozière et al. 2015). In a nutshell, a QCM measures the mass difference per unit area by recording the change in resonant frequency of a built-in quartz crystal resonator. The transduced signal (ΔF) represents the measured frequency change (Hz), which is based on a physical phenomenon called the converse piezoelectric effect. Piezoelectricity is generated on opposite surfaces of a crystalline material upon mechanical deformation (e.g. pressure or torsion) of the crystal along a given direction. Among the many types of crystals that exhibit piezoelectricity, quartz exceptionally possesses the desired chemical, electrical, mechanical, and thermal properties and is thus used as the crystal in QCM systems. To make the best use of QCM, exquisite design on the chip is needed to functionalize the electrode with a variety of surface chemistries and modifications for molecular recognition (Cheng et al. 2012). Modern ionic liquids are a class of materials that are composed solely of anions and cations that are relatively large in molecular structure. The unique chemical and physical properties of ionic liquids have made them widely accepted in technological applications such as nonvolatile plasticizers, thermo and hydraulic fluids, high- and low-temperature lubricants, electrochemical cells and devices, media for various chemical reactions, as well as carbon quantum dots (Wang et al. 2015). Membrane-free microelectrode modified with a thin layer of room-temperature ionic liquid for gas sensor design has also been described (Buzzeo et al. 2004). This review describes the exploration of functionalized SILs for the detection of VOCs. The method is chemical reaction based and is specific to functional groups (such as aldehyde) present in gas molecules. A 9 MHz QCM apparatus was used to develop the integrated system equipped with ionic liquids tailored for reaction-based gas sensing.

Gas sensing technology

Conductivity gas sensors

Among conductivity sensors, metal-oxide semiconductors are one of the most common sensing materials due to its low cost and good sensitivity (Fine et al. 2010). The principle of detection is through redox reactions between the oxide surface and the target gas, where the electronic variation on the oxide surface is transduced into an electrical resistance variation. Depending on the transducer, the difference of resistance can be determined by the change of capacitance, mass, optical characteristics, reaction energy, or work function. Metal oxides (SnO_2, CuO, Cr_2O_3, V_2O_5, WO_3, and TiO_2) have been used to detect combustible, oxidizing, or reducing gases such as carbon monoxide, hydrogen, liquid petroleum gas, methane, and nitrogen oxide (Batzill and Diebold 2005). Although some metal-oxide semiconductors show good sensitivity, they may also suffer from poor response linearity and selectivity due to the interference of other gases. In addition, most metal-oxide gas sensors require high operating temperature (up to 500°C) to reach the optimal reaction temperature for the target gas (Berger et al. 2009). The sensing material has to be preheated to enhance the adsorption of gas molecules on the sensing surface, which has limited the application

of metal-oxide gas sensors. Another major problem is the long recovery time that makes it unpractical for the development of electronic noses. In general, metal-oxide gas sensors exhibit drastically greater sensitivity to inorganic gases and a few VOCs such as ethanol and formaldehyde. However, it has been demonstrated that the indiscriminate response of methyl, ethyl, isopropyl, and butyl alcohols on SnO_2 films reflects the major challenges in gas sensing using metal-oxide semiconductor devices (i.e. selectivity and response time; Wang and Hu 1999). In addition, many other VOCs that result in health problems can not be detected by metal-oxide gas sensors effectively (Liu et al. 2012).

In contrast, conducting polymer-based gas sensors are frequently used to detect a wide range of gases such as VOCs, aromatic volatiles, and halogenated compounds. The organic gas sensing polymer composite may be spray, spin, or dip coated onto the sensor, which typically has two electrodes that are fabricated on an insulating polymer. Upon exposure to a gas, the physical properties of the insulating substrate changes due to the absorption of volatile molecules. The signal transduction mechanism can be described by London dispersion, dipole/induced dipole interactions, dipole/dipole interactions, and hydrogen bonds, in which responses are normally measured as the relative differential resistance. Polyaniline, polypyrrole, polythiophene, and their derivatives are typical organic conducting polymers that have been investigated for gas sensing, in which the doping process is required to increase conductivity by redox reactions or protonation (Bai and Shi 2007). Polymer-based gas sensors have several advantages for gas detection, including high sensitivity and short response time. Moreover, although operating temperatures of metal-oxide gas sensors are usually more demanding, polymer-based sensors operate at room temperature. However, polymer composites are also sensitive to temperature fluctuations that may result in variation of sensor responses and thus output errors in the system.

Spectroscopic gas sensors

Spectroscopic instruments generally have higher sensitivity, selectivity, and stability than other gas sensing devices because of their delicate set-up of instrumentation, which also comes with price. If miniaturization and cost are not to be taken into consideration, some spectroscopic methods represent an excellent alternative for accurate gas detection. The performance of an instrument should be less deteriorated by environmental factors and its relatively shorter response time makes online real-time detection possible in some cases. Spectroscopic gas analysis is mainly based on absorption and emission spectrometry. The principle of absorption spectrometry is the Beer Lambert law, which states that differential optical absorption spectroscopy, Raman light detection and ranging, tunable diode laser absorption spectroscopy, etc., have been developed. One of the most commonly used on-site methods for the continuous monitoring of airborne VOCs is differential optical absorption spectroscopy. It has the advantages of fast response time and low limit of detection but also has the disadvantage of optical interference from oxygen, ozone, and several hydrocarbons (Skov et al. 2001). The theory of emission spectrometry is that excited atoms emit photons and then return to its ground state; laser-induced breakdown spectroscopy is one example. Interestingly, Fourier transform infrared spectroscopy can be used in either absorption or emission spectrometry such as nondispersive infrared and quantum cascade laser gas sensors for the latter (Arunajatesan et al. 2007).

Traditional analytical instruments have been used for gas detection such as MS and GC. MS via direct injection is frequently used for the detection of VOCs. To enhance the sensitivity required for the identification of trace levels of VOCs, tandem mass analysis is typically employed. Ions of a particular mass-to-charge ratio are selected first and then subjected to the next stage for further fragmentation. The fragmented daughter ions are analyzed without interference of a large amount of unrelated parent fragments and thus beneficial for the detection of trace gases in complex mixtures. For example, proton transfer reaction MS (PTR-MS) is among the techniques that have been used extensively for the online analysis of VOCs (Lindinger et al. 1998). The PTR-MS technique offers rapid and accurate measurement of VOCs with a very low limit of detection. However, isomeric and isobaric compounds are not able to be separated and measured individually by PTR-MS instruments. On the contrary, GC in conjunction with flame ionization detection, MS, or photoionization has been used for VOC detection such as in the food industry (Afoakwa et al. 2009). GC is used for analyte separation, whereas the coupled detector is for the measurement of separated analyte. These GC-related methods normally use batch detection that involves analyte sampling, transportation, pre-concentration, and finally separation via chromatography before data analysis. These methods are useful for trace VOC detection, but they are time and labor consuming. In addition, the concentration detected from such analysis is the average or accumulated level rather than spatial variations over the sampling time period.

Piezoelectric sensors

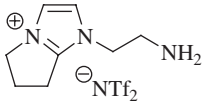
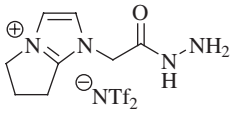
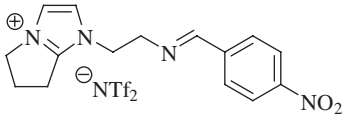
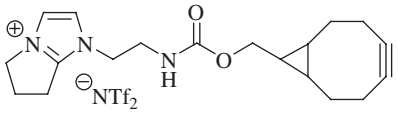
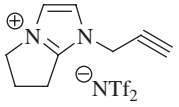
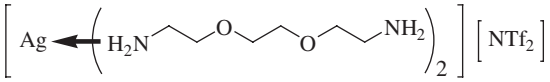
Sensors based on piezoelectric transducers are pressure or mass sensitive. A typical piezoelectric gas sensor is composed of a substrate of quartz that is cut at a crystalline angle to support a gas-sensitive material that is coated on the quartz surface. QCM and SAW devices are two representative microbalance sensors that the former employs a bulk acoustic wave sensor, whereas the latter uses a SAW sensor. Sensing materials such as nonconducting polymers can be coated on QCM and SAW sensors to capture the analyte of interest. The piezoelectric quartz converts acoustic waves to electric signals. When the sensing material adsorbs specific molecules, the mass of the coated material increases and causes the acoustic waves to travel slower. This subtle change in mass can be detected by the sensor microelectronics once the acoustic wave is converted to an electric signal. The signal response varies in physiosorption and chemisorption. CNTs (Penza et al. 2005), ionic liquids (Kubersky et al. 2015), molecular imprinted polymers (Matsuguchi and Uno 2006), PVC-blended lipids (Shafiqul Islam et al. 2005), and syndiotactic polystyrene semicrystalline (Mensitieri et al. 2003) have been used to coat on QCM sensors and have enabled the detection of a variety of pollutants and the sensing of VOCs. Temperature and humidity control are the major issues for accurate detection, as the resonant frequency is affected by those factors in this type of gas sensors. Therefore, modifications in coating materials have been the focus to improve the sensitivity and specificity in gas sensing. Some commercial QCM sensor systems are available for moisture and inorganic gas detection, but the detection for VOCs is rare and sensitivity is typically in the range of 10–10^3 ppm, which is not good enough for trace-level detection (Si et al. 2007).

Gas sensing based on ionic liquids

Gas analysis can be widely applied in environmental monitoring and human health-care. However, a sensitive and specific gas sensing technique that can provide the most detailed information on sample composition is still on demand. Among those important in sensor development for commercial purposes, the GC-MS requires expensive instrumentation and skilled analysis. Moreover, it is difficult to detect the lowest molecular weight VOCs such as formaldehyde and ammonia. Organic polymer and metal-oxide adsorbent array are often nonspecific and exhibit poor selectivity for detection of gas samples. In addition, solid-state sensors are not sensitive enough. Therefore, a new series of chemoselective SIL-based QCM gas analysis system have been continuously developed in our laboratory since its first publication in 2010 (Table 1). This SIL-on-QCM chip system not only is a cost-effective approach but also shows a great potential to detect a wide range of VOCs with high efficiency and specificity.

In combination, the tunable chemical reactivity, negligible volatility, and good thermal stability of ionic liquids with high sensitivity of QCM chips make this integrated platform highly attractive for chemoselective gas sensing. Especially, the negligible vapor pressure of ionic liquids ensures that the sensors do not “dry out” on QCM chips and shows free of leakage and the loss of loading during the measurement. As illustrated in Figure 2, when gases rapidly diffuse into the SIL thin film on QCM chips, specific chemical reactions for selective gases in ionic liquids occur under appropriate experimental conditions. The mass changes on QCM chips during the chemical reactions of a gas analyte and the tailored ionic liquid are readily obtained and ultimately transduced to generate an analytical signal. The thin coatings (200–300 nm thickness) of ionic liquids on the surface of the QCM chip (9 MHz) are achieved by depositing the diluted methanol containing SILs. The used SIL layer on QCM chip could be easily washed away by methanol and further replaced with a new SIL. This regenerable SIL-on-QCM chip system

Table 1: Structures of SILs.

SIL	Structure
SIL 1	
SIL 2	
SIL 3	
SIL 4	
SIL 5	
SIL 6	

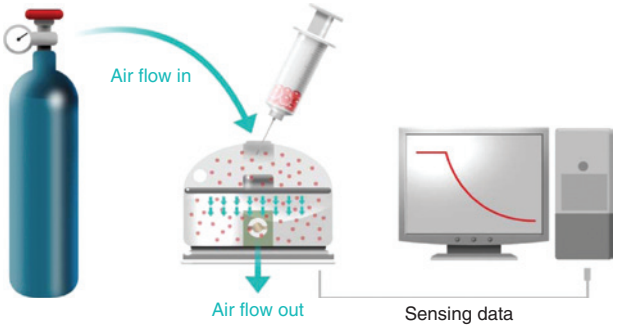


Figure 2: Schematic representation of a SIL-on-QCM gas analysis system for chemoselective gas sensing by specific chemical reactions.

can be performed at room temperature and dried ambient air is used as carrier gas.

SIL 1 was first synthesized to detect aldehyde/ketone gases in 2010 (Tseng and Chu 2010). However, the results showed that **SIL 1** was more sensitive and selective to capturing aldehyde than ketone gases. To improve the sensitivity of ketone gas sensing, **SIL 2** was synthesized afterwards (Liu et al. 2013). During the chemical reactions, **SIL 1** and **SIL 2** formed the imine and hydrazone adducts with aldehydes and ketones, respectively (Figure 3). **SIL 1** displayed a similar reaction rate to aliphatic and aromatic aldehydes, and **SIL 2** reacted efficiently with acyclic and cyclic ketone gases. It is noted that the irreversible nature of the frequency drops from QCM measurements of aldehyde and ketone sensing by both SILs indicated a nonequilibrium formation of Schiff bases. It is also worth mentioning that this SIL-on-QCM chip system was totally insensitive to common VOCs such as methanol, ethanol, ethyl acetate, hexane, and, most significantly, moisture (water; ΔF=0 Hz); that is, any water present in the gas stream would not be in any direct competition with detecting gases. Encouraged by the results of sensing aldehyde/ketone gases, **SIL 3** was specially synthesized to detect amine gases. The chemical reaction between **SIL 3** and amine gases was based on the transimination reaction. Although the model amine gas (propylamine) was detectable at low concentration (28.5 ppb), the minimal QCM response (~0.5 Hz) and seemly reversible in its signal were noticed. From a quick search of the literature, we realized that Lewis acids could notably facilitate the transimination reaction as well as imine and hydrazone forming reactions in conventional molecular solvents. We found that **SIL 3** with 1 mol% hint of $Sc(OTf)_3$ could catalyze

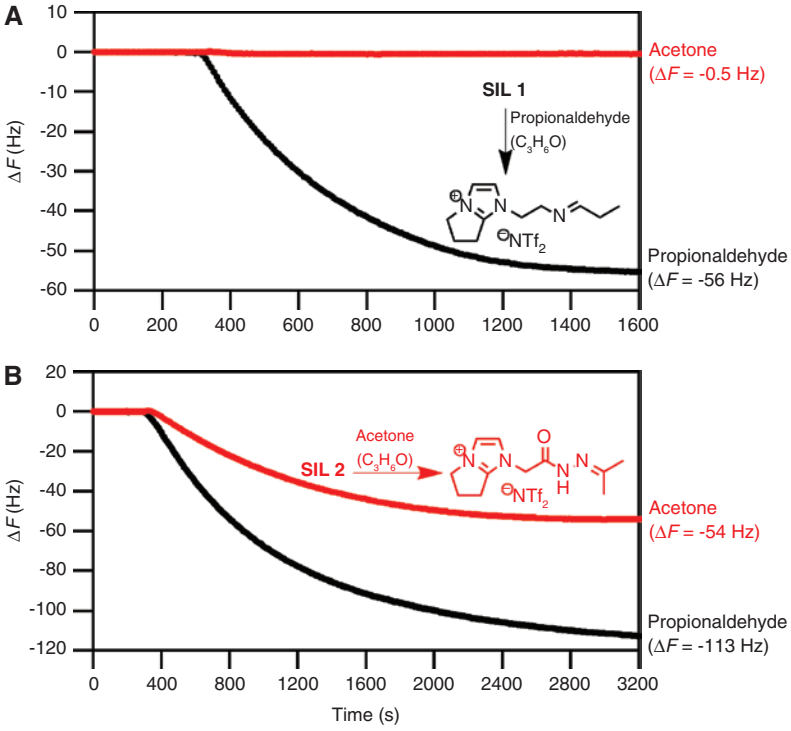


Figure 3: Chemoselective detection of acetone and propionaldehyde gases (98 ppb each) of identical molecular weight (C_3H_6O) by 9 MHz QCM thin coated with (A) **SIL 1** and (B) **SIL 2** (3.3 nl each, 300 nm thickness).
Air was used as the carrier gas with a flow rate of 3 ml/min and gas samples were injected at 300 s. The resonance frequency drop (ΔF) is the QCM response on the quartz chip surface.

the transimination reaction to produce the largest and irreversible QCM response (ΔF=20 Hz). The sensitivity of detection was also significantly improved about 11.4-fold for the model amine gas (28.5 ppb→2.5 ppb). Most remarkably, even the smallest molecular weight amine gas, ammonia, the detection limit could be achieved approximately 3.9 ppb (ΔF=1.0 Hz). With this in mind, we could expect to develop an ultrasensitive SIL for the detection of ketone gases. Indeed, **SIL 2** with 2 mol% of $Sc(OTf)_3$ also could promote hydrazone formation and produce 2-fold increase and irreversible QCM response. With the addition of metal triflate, the detecting sensitivity of **SIL 2** was significantly down to 0.6 ppb for cyclohexanone and 1.1 ppb for acetone. To our surprise, even the masked ketone gases such as 2,2-dimethoxypropane was also detectable at a level of 34 ppb.

Since the success of SIL-on-QCM chip system in the detections of aldehyde, ketone, and amine gases, we next turned our attention to the SIL detection of azide gases. Based on the recent advances of click chemistry, the Huisgen 1,3-dipolar azide and alkyne [3+2] cycloaddition, we synthesized **SIL 4** and **SIL 5** for the chemoselective detection of organic azide gases (Tseng and Chu 2014). Compared to the unstrained **SIL 5**, we can expect that the strained **SIL 4** should possess much greater enhancement in reactivity toward organic azides. Indeed, **SIL 4** shows high sensitivities toward both aliphatic and aryl azide gases, but **SIL 5** was totally inert toward azide gas sensing (Figure 4). Among all azide gases investigated, the sensitivity of detection was 5 ppb for benzyl azide and 35 ppb for butyl azide. It is noted that the reactivity order of benzyl azides>phenyl azides>allyl azides towards **SIL 4** could be understood by the reported activation energy (Garcia-Hartjes et al. 2013). In addition, **SIL 4** could be applied to detect azide gases with dual functional groups such as 2-azioethyl amine. Most remarkably, **SIL 4**, which carries a reactive alkyne dienophile group, can also readily capture cyclopentadiene gas at low ppb (65.5 ppb) through the Diels-Alder [4+2] cycloaddition reaction (Tseng and Chu 2014). Namely, **SIL 4** based on cycloaddition reactions is well suited to detect both azide and diene gases with a high sensitivity.

To further develop a robust SIL-on-QCM chip system with superior selectivity and sensitivity at low cost, our laboratory continuously investigates potential techniques to improve SILs at all aspects. Recently, transition metal-containing ionic liquids have received significant research attention. Due to the strong affinities between transition metal ions and neutral alkylamines, transition metal-containing ionic liquids can be easily prepared under convenient reaction conditions (e.g. aqueous solution and room temperature) with high efficiency. Furthermore, there is no tedious organic synthesis steps involved but only simply sample mixing followed by straightforward extraction workups. Thus, we synthesized a new transition metal-containing ionic liquids, **SIL 6**, for detecting exclusively aldehyde gases from an inexpensive and commercially available alkylamine, 1,2-bis(2-aminoethoxy) ethane, as the ligand for silver (I) (Li et al. 2015). Unlike the synthesis of imidazolium-based **SIL 1** (Tseng and Chu 2010) that required four synthetic steps with a low yield (37%), the preparation of **SIL 6** could be achieved by only straightforward mixing of silver and amine reagents with a moderate high yield (66%). In our hand, **SIL 6** was totally insensitive to the ketone gases. Notably, with the same concentration of model aldehyde gas (propionaldehyde, 100 ppb), **SIL 6** displayed a stronger QCM response (ΔF=-40 Hz) than **SIL 1** (ΔF=-19 Hz; Figure 5). Although silver ionic liquids have apparent but inherent drawback that they are less stable towards light, they process

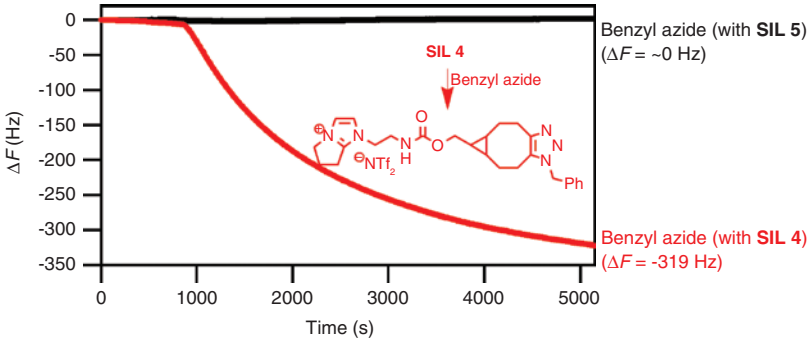


Figure 4: Chemoselective detection of benzyl azide gas (146 ppb) by 9 MHz QCM thin coated with **SIL 4** and **SIL 5** (3.3 nl each, 300 nm thickness).
Nitrogen was used as the carrier gas with a flow rate of 3 ml/min and gas samples were injected at 1000 s. The resonance frequency drop (ΔF) is the QCM response on the quartz chip surface.

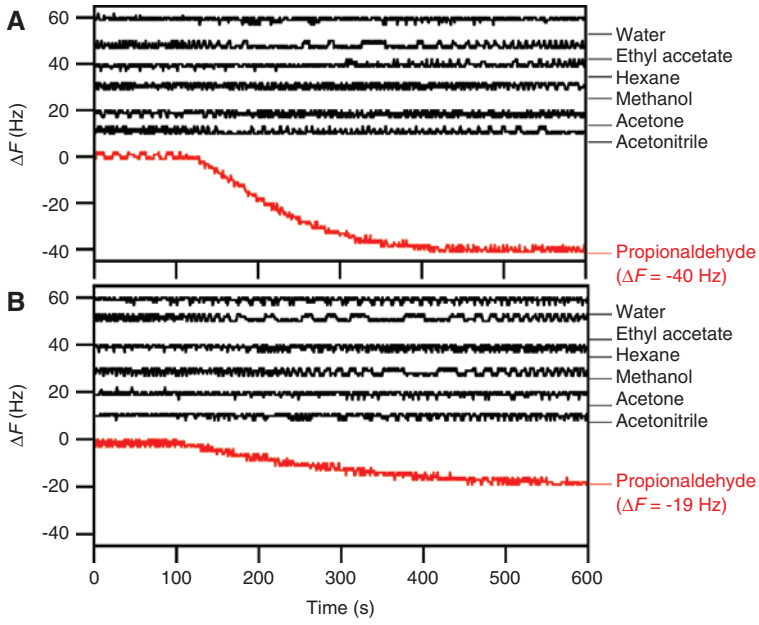


Figure 5: Chemoselective detection of water, ethyl acetate, hexane, methanol, acetone, acetonitrile, and propionaldehyde gases (100 ppb each) all by a multichannel QCM thin coated with (A) **SIL 6** and (B) **SIL 1** (33 nmol each, 200–300 nm thickness).
The QCM sensograms for water, ethyl acetate, hexane, methanol, acetone, and acetonitrile gases were vertically shifted (10 Hz in between) for clarity. Nitrogen was used as the carrier gas with a flow rate of 3 ml/min, and gaseous samples were injected at 100 s. The resonance frequency drop (Δ*F*, in Hz) is the QCM response on the quartz chip surface.

many advantages such that only minute amounts of SILs (10–15 nl/quartz chip) are consumed. In addition, no chemical immobilization on quartz chips is needed, plus they can be readily regenerated by simply washing them away. Finally, the SIL platform developed in this work is highly chemoselective (**SIL 1** and **SIL 6**: specific to aldehyde, **SIL 2**: sensitive to ketone, **SIL 3**: specific to amine, and **SIL 4**: selective to azide gases) with superior gas reactivity for **SIL 6** than the imidazolium-based **SIL 1** and, most significantly, totally insensitive to moisture.

Conclusions and outlook

The real-time detection of man-made or naturally occurring VOCs is a critical and challenging task for environmental monitoring and disease diagnosis. Gas sensing systems based on different principles have been developed to convert gaseous analytes into readable output signals. However, many gas sensors, such as metal-oxide semiconductors, suffer from high operating temperature that is impractical and has limited its applications. The electromechanical device QCM represents an excellent platform if sensitive, selective, and versatile sensing materials were available. To this end, we have developed a series of ultrasensitive SILs that are capable of detecting VOCs selectively. SIL-on-QCM detects VOCs by sensing normally neglected changes in weight on a nanogram level. Target analytes are captured by SILs and the accumulated weights are transduced into frequency shifts on QCM. According to the aforementioned advantages, the tunability and structural diversity make SILs promising for the creation of a pattern recognition library of chemical sensor arrays. An integrated multichannel system could be designed to efficiently detect and optimally exploit the advantages of various SILs for various VOC sensing simultaneously in the future. Although it remains a long way before a gas sensing system could function as good as a dog's nose, we envision developing a collection of SIL-on-QCM and even hybrid gas sensing systems that will pave the way for complex VOC detection in the fields of environmental monitoring and disease diagnosis.

In addition to the inherent light instability of silver ionic liquids recently developed in our laboratory (Li et al. 2015), temperature and humidity control are other major issues for accurate detection, as the resonant frequency is affected by those factors in this type of gas sensors.

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