Chemoselective gas sensing ionic liquids

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Scheme S1. Synthesis of SILs 1 and 2.
**Scheme S2.** Schematic representation of the 9 MHz QCM gas analysis system used in this study.
Scheme S3. Proposed mechanism for the Sc(OTf)₃-catalyzed transimination reaction exploited for amine gas sensing by SIL 2 using QCM.
Figure S1. Chemoselective detection of propionaldehyde and acetone gases, and the acid-base neutralization of formic acid gas, by SIL 1 using 9 MHz QCM, respectively. Overlaid sensorgrams of reactions of propionaldehyde, acetone, water and formic acid gases with SIL 1 (3.3 nL) thin-coated on QCM quartz chip (300 nm thickness). All gases studied have identical concentration (412 ppb). In terms of detection selectivity and sensitivity, aldehyde outperformed ketone in reaction with SIL 1. Moreover, upon acid-base titration, this SIL on QCM chip reacted instantaneously with the organic acid gas; that is, an ultrafast (“free fall”) drop in QCM resonance frequency was observed. As resonance frequency drop, $\Delta F$ is the QCM response on the chip surface.
Figure S2. Chemoselective detection of formaldehyde gas by SIL 1 using 9 MHz QCM. (A) Overlaid sensorgrams of reactions of formaldehyde gas (3.8, 7.6, and 11.4 ppb) with SIL 1 (3.3 nL) thin-coated on QCM quartz chip (300 nm thickness). (B) A plot of $\Delta F$ (Hz) vs. gas concentration (ppb) in the QCM chamber. As resonance frequency drop, $\Delta F$ is the QCM response on the chip surface. At $\Delta F = -1.0$ Hz, using our QCM instrument, the sensitivity of detection was approximately 8.4 ppb for formaldehyde.
Figure S3. Chemoselective detection of ammonia gas by SIL 2 using 9 MHz QCM. (A) Overlaid sensorgrams of ammonia (0, 2.4, 4.8, 7.2, 12, 16.8, 33.6, 50.4, 84, and 117.6 ppb) reactions with SIL 2 or [b-3C-im][NTf$_2$] (10 nL) thin-coated on QCM quartz chips (909 nm thickness). Only the sensorchip coated with SIL 2 containing 1 mol% Sc(OTf)$_3$ permits the detection of ammonia gas. As a control experiment, in the presence of 1 mol% Sc(OTf)$_3$, ammonia gas neither reacts with nor non-specifically adsorbs [b-3C-im][NTf$_2$] ionic liquid coated on QCM chip. (B) A plot of $\Delta F$ (Hz) vs. gas concentration (ppb) in the QCM chamber. As resonance
frequency drop, $\Delta F$ is the QCM response on the chip surface. At $\Delta F = -1.0$ Hz, using our QCM instrument, the sensitivity of detection was approximately 3.9 ppb for ammonia gas.
Table S1. Screening of metal triflates as catalysts for transimination reaction of propylamine gas (28.5 ppb) with SIL 2 (10 nL, 909 nm thickness) on a QCM chip.

<table>
<thead>
<tr>
<th>Metal triflate (1 mol%)</th>
<th>ΔF (Hz)</th>
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<tr>
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<tr>
<td>Al(OTf)$_3$</td>
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<td>Yb(OTf)$_3$</td>
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</table>
Synthesis of SIL 1

To a solution of 2-bromoethylamine hydrobromide (1.0 g, 4.88 mmol) and triethylamine (1.5 g, 14.85 mmol) in dichloromethane (20 mL), benzyl chloroformate (1.3 g, 7.62 mmol) was added portion-wise at 0 °C. The resultant mixture was stirred at 0 °C for 2 h. The mixture was then washed with sodium bicarbonate (10%, 3×10 mL) and citric acid (10%, 3×10 mL) and dried over anhydrous sodium sulfate. Solvent was evaporated to obtain crude product. The residue was then purified by silica gel column chromatography with ethyl acetate/hexane (1/7, v/v) as the eluent to afford the pure product (1.2 g, 96 % yield) as a white crystal solid.

6,7-dihydro-5H-pyrrolo[1,2-\(\alpha\)]imidazole was prepared as described previously.\(^1\) To a round-bottomed flask containing 6,7-dihydro-5H-pyrrolo[1,2-\(\alpha\)]imidazole (130 mg, 1.20 mmol) was added \(N\)-benzyloxycarbonyl-2-bromoethylamine (350 mg, 1.36 mmol). The mixture was stirred and heated at 80 °C for 2 h. The crude product was then purified by silica gel column chromatography with methanol/dichloromethane (1/10, v/v) as the eluent to afford the desired product (411 mg, 94% yield) as a colorless viscous liquid.

A mixture of bistrifluoromethanesulfonimide lithium salt (411 mg, 1.12 mmol), water (5 mL) and the bromide salt (355 mg, 1.24 mmol) was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was added dichloromethane (10 mL) and then washed with water (3×3 mL). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography with ethyl acetate/ dichloromethane (1/3, v/v) as the eluent to afford
the pure product (455 mg, 72 % yield) as viscous liquid.

The Cbz-protected ionic liquid (200 mg, 0.35 mmol) was then dissolved in methanol (5 mL) and catalytic amount of Pd(OH)₂/C was added. The resulting mixture was bubbled with hydrogen. Reaction was carried out at room temperature for 1 h. Pd(OH)₂/C was filtered off, and the methanol was removed under reducing pressure to give the desired product SIL 1 (150 mg, 98% yield) as viscous liquid. ¹H NMR (400 MHz, CDCl₃) δ 2.66 (qn, \( J = 7.2 \text{ Hz}, \text{CCH}_2\text{C}, 2\text{H} \)), 3.02 (t, \( J = 5.3 \text{ Hz}, \text{NCH}_2\text{C}, 2\text{H} \)), 3.16 (t, \( J = 8.0 \text{ Hz}, \text{N}=\text{CCH}_2, 2\text{H} \)), 4.11 (t, \( J = 5.4 \text{ Hz}, \text{NCCH}_2, 2\text{H} \)), 4.19 (t, \( J = 7.2 \text{ Hz}, \text{NCH}_2, 2\text{H} \)), 7.63 (s, 2C=CH₂, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 23.0, 25.7, 40.5, 48.0, 49.7, 118.1, 121.1 (q, \( J_{\text{CF}} = 318 \text{ Hz}, \text{CF}_3 \)), 125.9, 153.2; FAB-HRMS m/z [M]⁺ calcd for C₈H₁₄N₃ 152.1188, found 152.1191.

**Synthesis of SIL 2**

To a round-bottomed flask containing SIL 1 (75 mg, 0.17 mmol) was added 4-nitrobenzaldehyde (37 mg, 0.25 mmol) and Na₂SO₄ in dichloromethane (2 mL). The solution was allowed to stand at room temperature for 8 h. The mixture was filtered to remove the sodium sulfate and the filtered solution was concentrated under vacuum. The residue was washed with ether to remove excess 4-nitrobenzaldehyde. The viscous liquid was dried under vacuum to afford the pure product SIL 2 (75 mg, 76% yield) as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 2.63 (qn, \( J = 7.5 \text{ Hz}, \text{CCH}_2\text{C}, 2\text{H} \)), 3.15 (t, \( J = 7.6 \text{ Hz}, \text{N}=\text{CCH}_2, 2\text{H} \)), 4.01 (t, \( J = 5.3 \text{ Hz}, \text{NCCH}_2, 2\text{H} \)), 4.19 (t, \( J = 7.2 \text{ Hz}, \text{NCH}_2, 2\text{H} \)), 4.45 (t, \( J = 5.7 \text{ Hz}, \text{CH}_2, 2\text{H} \)), 7.64 (d, \( J = 14.8 \text{ Hz}, 2\text{C}=\text{CH}, 2\text{H} \)), 7.97 (d, \( J = 8.6 \text{ Hz}, \text{ArH}, 2\text{H} \)), 8.31 (d, \( J = 8.6 \text{ Hz}, \text{ArH}, 2\text{H} \)), 8.49 (s, CH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 23.0, 25.8, 48.1, 49.1, 59.2, 118.1, 121.1 (q,
$J_{CF} = 318$ Hz, CF$_3$, 124.2, 126.2, 129.2, 141.2, 149.0, 152.9, 162.5; FAB-HRMS m/z [M]$^+$ calcd for C$_{15}$H$_{17}$N$_4$O$_2$ 285.1352, found 285.1352.

References:

QCM measurements

The PSS QCM system (9 MHz) was operated under room temperature and using air as carrier gas. The flow rate of the carrier gas was controlled by a commercial flow meter (Supelco Inc.). The organic vapor steams were obtained by gasifying the chemicals in the sealed glass container (1.26 L). A rapid initial frequency decrease was typically observed within 5 sec after organic vapor was injected into the flow chamber. The QCMs employed 9-MHz AT-cut quartz deposited with gold electrodes (area 11 mm²) on both sides were commercially available (ANT Tech, Taipei, Taiwan). Before use, the surfaces of gold electrodes on chips were cleaned with NaOH (2 N) for 30 min, water for 10 min, and HCl (1 N) for 5 min in order to remove organic adsorbent impurity form gold surfaces. The chips were then rinsed with water thoroughly. The cleaned quartz chips were dried under nitrogen.

A solution (1 L) of the SIL 1 (1/300, v/v) in methanol was applied to the cleaned bare gold electrode to give an amine SIL 1 surface. The chip was placed in a heating oven to remove the remaining methanol. This freshly prepared sensor chip was then mounted in the flow chamber (77 cm³) and used air as carrier gas at flow rate of 3.0 mL/min. A numbers of target organic vapor steams (412 ppb), propionaldehyde, benzaldehyde, acetone, ethyl acetate, formic acid, methanol, water and hexane, were injected into the chamber, respectively.

Quantitative measurement of butyraldehyde and 2-butanone

A freshly prepared SIL 1 chip was set in the flow chamber and using air as carrier gas
at flow rate of 3.0 mL/min. A series dilution of butyraldehyde (7.6 – 53.2 ppb) and 2-butanone (60.8 – 150.5 ppb) were injected into the chamber. The frequency changes of the QCM responding to the different concentrations of target gas were recorded with time.

**Detection of amine gas**

An acetonitrile solution (1 L) containing SIL 2 (1/100, v/v) and 1 mol% Sc(OTf)₃ was applied to the cleaned bare gold electrode to give an imine SIL 2 surface. Then the chip was placed in a heating oven to remove the remaining solvent. This freshly prepared sensor chip was then mounted in the chamber and used air as carrier gas at flow rate of 3.8 mL/min. Propylamine (28.5 ppb) was then injected into the flow chamber. The permanent frequency shifts versus time curves were recorded.

**Quantitative measurement of propylamine**

A freshly prepared sensorchip coated with SIL 2 containing 1 mol% Sc(OTf)₃ and a control chip coated with [b-3C-im][NTf₂] containing 1 mol% Sc(OTf)₃ were mounted into the chamber and flowing with air continuously until frequency had stabled under flow condition (3.8 mL/min). And then various concentrations of propylamine (17.1 – 119.7 ppb) were injected into the flow chamber. The frequency changes of the QCM responding to the different concentrations of target gas were recorded with time.

**Quantitative measurement of ammonia**
A freshly prepared sensorchip coated with SIL 2 containing 1 mol% Sc(OTf)₃ and a control chip coated with [b-3C-im][NTf₂] containing 1 mol% Sc(OTf)₃ were mounted into the chamber and flowing with air continuously until frequency had stabilized under flow condition (3.8 mL/min). And then various concentrations of ammonia (2.4 - 117.6 ppb) were injected into the flow chamber. The same concentration of H₂O steam was injected and no significant frequency changes were observed.
Footnotes

1. Simple aldehydes such as formaldehyde emitted from house construction materials or furniture can affect human health.


4. The acoustic decay lengths in 1-alkyl-3-methylimidazolium-based ionic liquids, [Rmim][NTf₂], at the 9 MHz QCM surfaces were calculated using the equation given below and found to be in the range of 930 nm—3.86 m (in water, δ ≈ 188 nm):

\[ \delta = \left( \frac{2 \eta}{\omega \rho} \right)^{1/2} \]

where \( \delta \), \( \eta \), and \( \rho \) are the decay length, the liquid density (1.394 g/cm³ for SIL-1), and liquid shear viscosity (34—83 cP), respectively, and \( \omega = 2 \pi f_s \) in which \( f_s \) is the QCM series-resonant frequency (L. A. Theisen, S. J. Martin and A. R. Hillman, *Anal. Chem.*, 2004, 76, 796.). All our QCM measurements involving the use of SILs thin-coated on chip surfaces (300 and 909 nm for SIL 1 and SIL 2, respectively) were within the range of acoustic decay lengths.
