

Electronic Supplementary Information

CO₂-triggered fine tune of electrical conductivity
via tug-of-war between ions

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Materials and Methods

Materials

3-Bromopropylamine hydrobromide and phthalaldehydic acid were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. 1-Methylimidazole was purchased from Acros Organics and used as received. Methanol, ethyl acetate, tetrahydrofuran (THF), dichloromethane, acetic acid, sodium hydroxide was purchased from Kanto Chemical Co., Inc. and used as received. Amberlite IRN 78A and aluminum oxide was purchased from Sigma-Aldrich Co., Llc. and used as received.

Synthesis of [C₃NH₂mim][*o*-aldBzCOO]

1-Methylimidazole (10.9 g, 133 mmol) was dissolved in 80 mL THF, and then 3-bromopropylamine hydrobromide (30.6 g, 140 mmol) was added to the solution under argon atmosphere. The mixture was refluxed at 90 °C for 5 h. After removing solvent, the solid was recrystallized in methanol/ethyl acetate mixture several times and dried under reduced pressure. The bromide anion was converted to hydroxide anion by stirring the bromide salt aqueous solution with Amberlite IRN 78A. After filtration, resulting liquid was neutralized by phthalaldehydic acid and then dried *in vacuo*. The resulting solution diluted with dichloromethane solution was passed through a column filled with aluminium oxide to remove excess amount of phthalaldehydic acid. The resulting solution was dried *in vacuo*. After drying, [C₃NH₂mim][*o*-aldBzCOO] was obtained as the ZI form.

^1H NMR (400 MHz; DMSO- d_6 ; Me $_4$ Si) δ = 9.62 (s, 1H, NCHN), 8.86 (s, 1H, N=CHC), 7.90 and 7.69 (t, J = 1.6 Hz, 2H, NCHCHN), 7.65-7.13 (m, 4H, protons of aromatic ring), 4.19 (t, J = 6.2 Hz, 2H, NCH $_2$ CH $_2$ CH $_2$ N=CH), 3.81 (s, 3H, NCH $_3$), 3.41 (t, J = 5.7 Hz, 2H, NCH $_2$ CH $_2$ CH $_2$ N=CH), 2.26-2.06 (m, 2H, NCH $_2$ CH $_2$ CH $_2$ N=CH). ^{13}C NMR (100 MHz; chloroform- d ; Me $_4$ Si) δ = 170.22, 138.29, 134.33, 129.69, 128.89, 127.36, 126.36, 124.22, 122.75, 56.75, 49.10, 46.87, 36.09, 30.39. Elemental analysis: [C $_3$ NH $_2$ mim][*o*-aldBzCOO]·2.2H $_2$ O (Found: C, 58.0; H, 6.6; N, 13.2. Calc. for C $_{15}$ H $_{21.4}$ N $_3$ O $_{4.2}$: C, 58.0; H, 6.9; N, 13.5%).

Structural shift of [C $_3$ NH $_2$ mim][*o*-aldBzCOO]

[C $_3$ NH $_2$ mim][*o*-aldBzCOO] (1.0 wt%) was added to ultrapure water. The pH of the solution was changed with 33 wt% NaOH solution and 25–100 wt% acetic acid solutions. The ratio of the IL form was confirmed by ^1H NMR. N $_2$ and CO $_2$ gas was saturated by water before passing the sample solutions to prevent evaporation of water of the samples; we confirmed that the volume of the sample solutions did not change before and after long-time gas bubbling.

Measurement of electrical conductivity of [C $_3$ NH $_2$ mim][*o*-aldBzCOO] solution

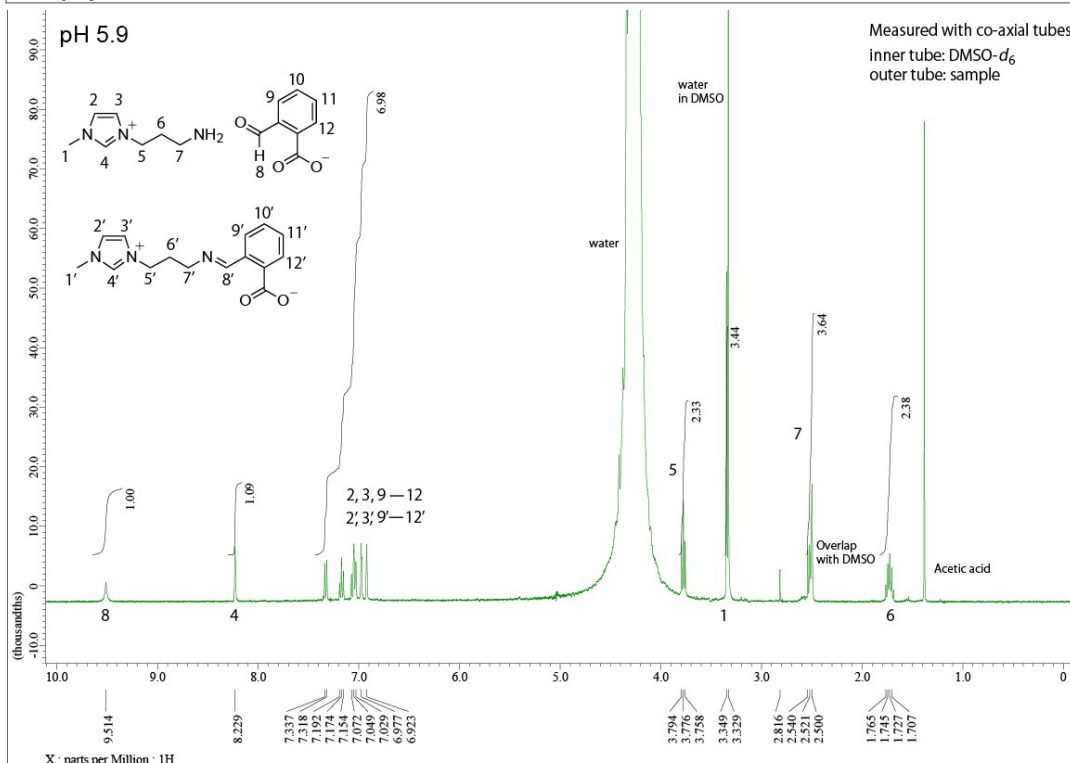
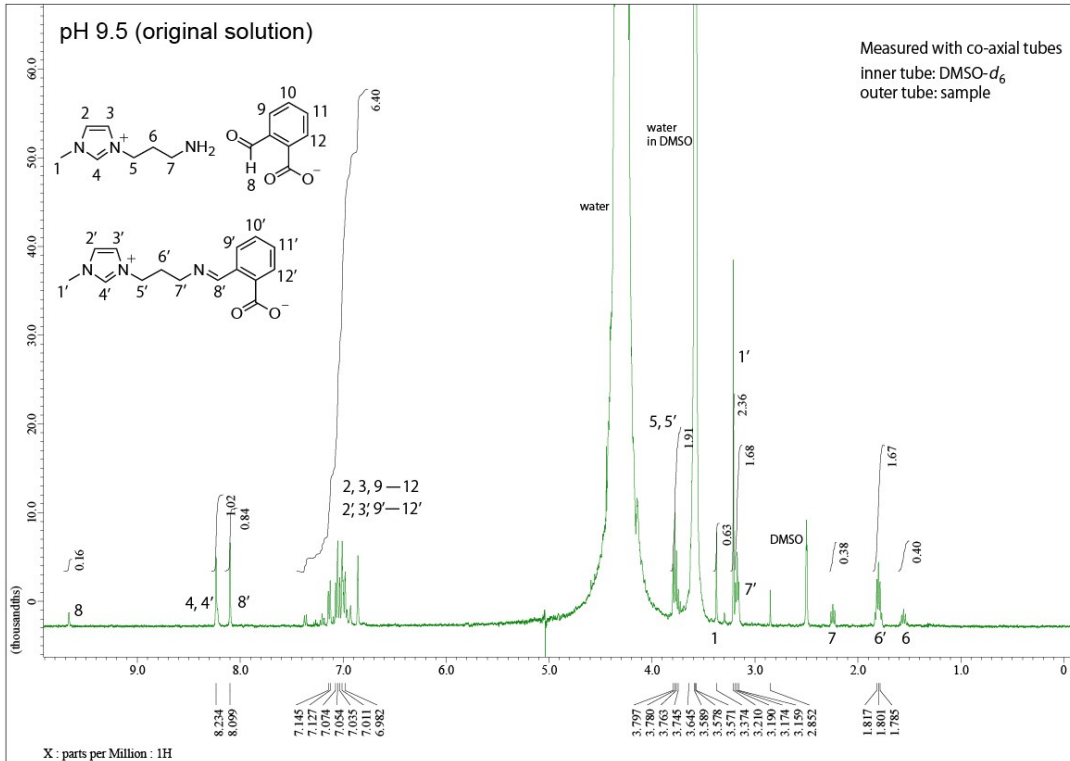
An electrical conductivity meter (LAQUA DS-72, Horiba Ltd.) was used for the measurement of electrical conductivity of the aqueous solution of [C $_3$ NH $_2$ mim][*o*-aldBzCOO]. The measurement was carried out after the 1.0 wt% solutions were bubbled

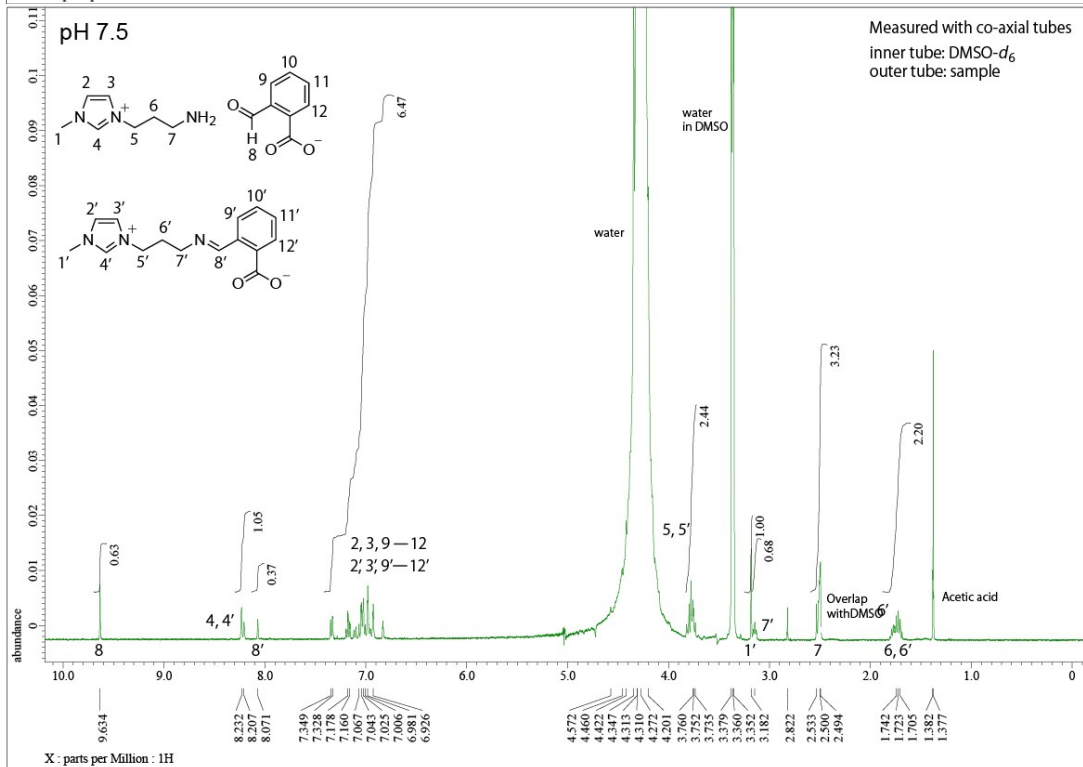
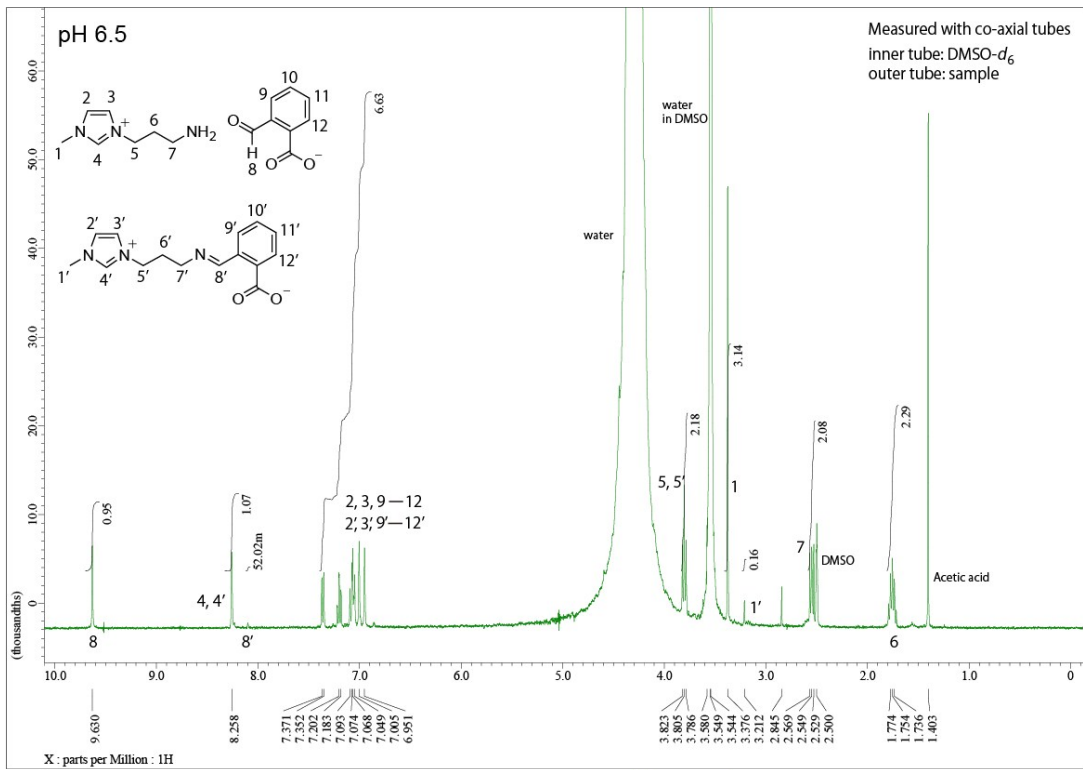
with N₂ or CO₂ until the electrical conductivity did not shift. N₂ and CO₂ gas was saturated by water before passing the sample solutions to prevent evaporation of water of the samples. The partial pressure of CO₂ was controlled using a controlling system (Multi-GAS 3000, Taitec corporation), by mixing with air.

Observation of emission from light-emitting diode (LED) incorporating a [C₃NH₂mim][*o*-aldBzCOO] solution as a variable resistor

The electronic circuit was prepared with a LED (HK-LED 5H(R), Asahi Electric CO. Ltd.), an alternating-current source (GW instek APS-7050, Texio Technology Corporation), and an ammeter (MT-4510, Mother tool Co. Ltd.). The 1.0 wt% [C₃NH₂mim][*o*-aldBzCOO] aqueous solutions (3 mL) were bubbled with 0.1 kPa of CO₂ for 20 sec. After LED was electrified (3.5 V, 45 Hz), the current value was measured and a picture was taken immediately. The same procedure was successively carried out with 1 and 101 kPa of CO₂. After that, the same procedure was conducted with N₂ for 16h. When the emission was controlled by exhaled breath, bubbling the breath was conducted for 3 min.

Supporting Figures





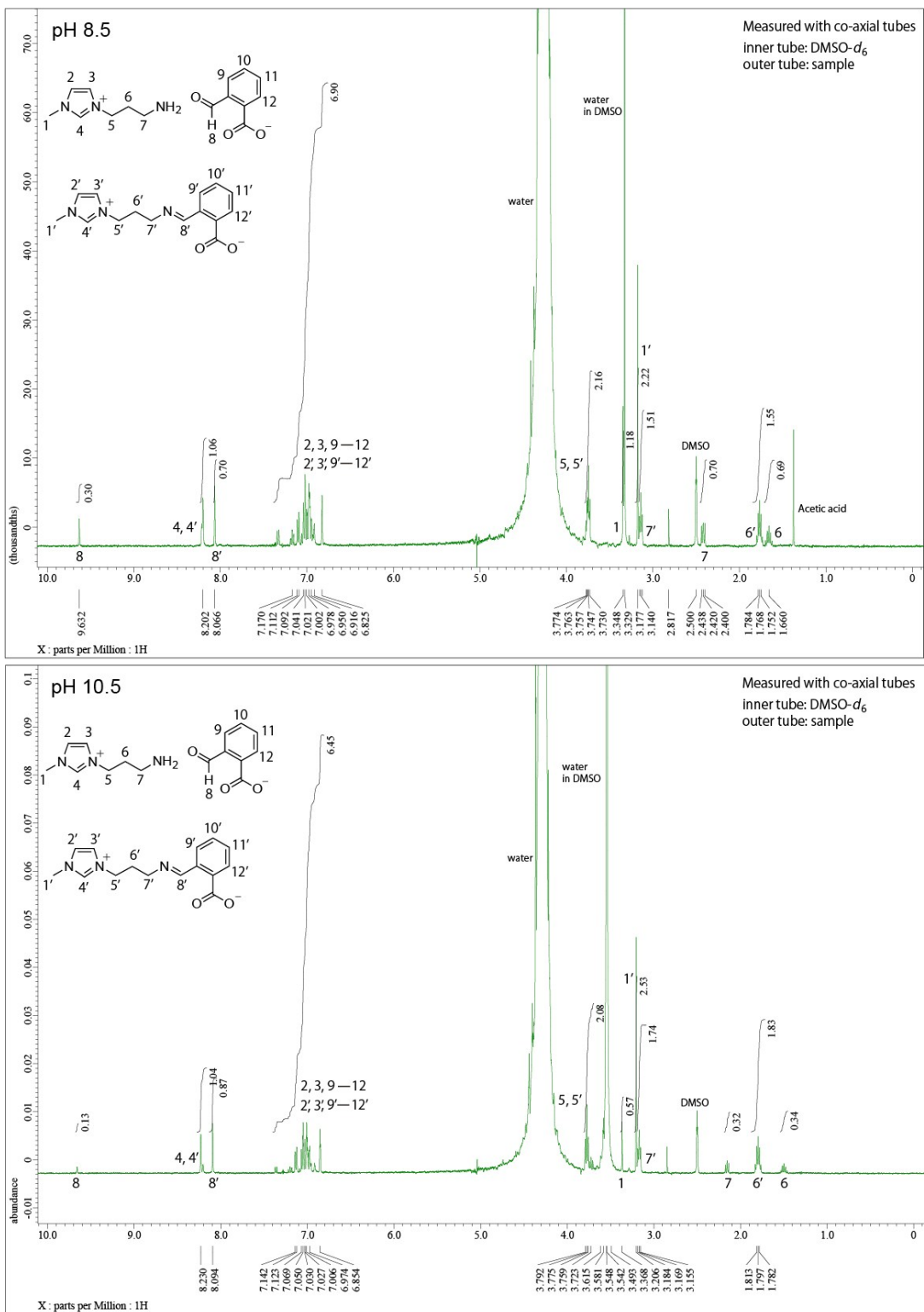


Fig. S1. ^1H NMR spectra of 1 wt% $[\text{C}_3\text{NH}_2\text{mim}][o\text{-aldBzCOO}]$ aqueous solution before and after changing pH by acid/base.

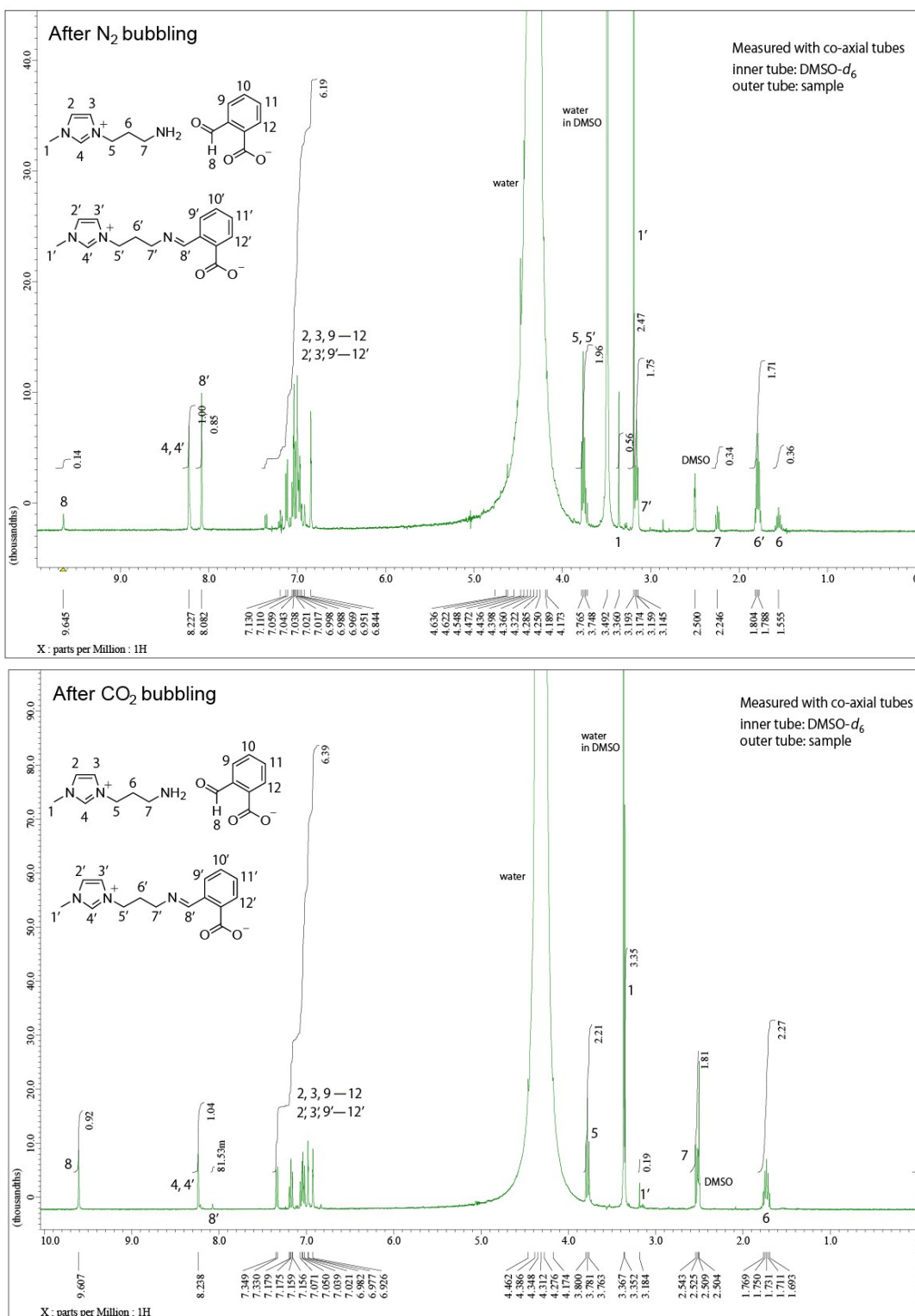


Fig. S2. ¹H NMR spectra of 1 wt% [C₃NH₂mim][*o*-aldBzCOO] aqueous solution after bubbling with (top) N₂ and (bottom) CO₂.

We subjected $[\text{C}_{3\text{NH}_2}\text{mim}][o\text{-aldBzCOO}]$ solution to mass spectrometry before CO_2 bubbling (Fig. S3a, b). Two small and large peaks were observed and attributed to the cation of the IL form ($m/z=140$) and ZI form ($m/z=272$) in positive mode because $[\text{C}_{3\text{NH}_2}\text{mim}][o\text{-aldBzCOO}]$ is a mixture of IL- and ZI form. ZIs are generally observed in mass spectra as proton-adducted form in positive mode because ZIs have single positive and negative charges and thus they are neutral in charge. Two large and small peaks were observed and attributed to the anion of the IL form ($m/z=149$) and ZI form ($m/z=270$, proton-abstracted form) in negative mode.

While the same peaks ($m/z=140$ and 272 in positive mode, $m/z=149$ and 270 in negative mode) were found after CO_2 bubbling (Supplementary Fig. S3c, d), but the peak height was different: the peak of IL form was higher than that of ZI form. This result clearly shows the exact structures of IL- and ZI forms and they shifted by bubbling with CO_2 .

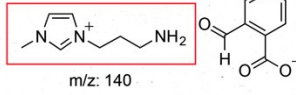
Some amines and ILs have ability to capture CO_2 via covalent bond. Then we have subjected the 1 wt% $[\text{C}_{3\text{NH}_2}\text{mim}][o\text{-aldBzCOO}]$ solution to mass spectrometry after CO_2 bubbling (Fig. S3c). If the cation reacts with CO_2 , the peak at 184 in m/z appears. However, no peak was observed at 184 and it shows the cation does not react with CO_2 . This strongly supports that CO_2 does not react with $[\text{C}_{3\text{NH}_2}\text{mim}][o\text{-aldBzCOO}]$ and consequently CO_2 works simply as an acid (H_2CO_3) in the solution.

(a)

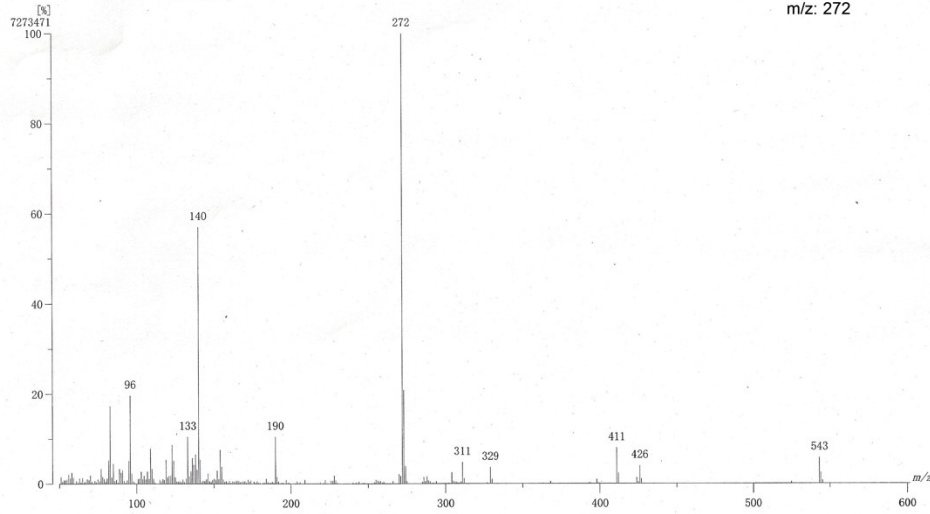
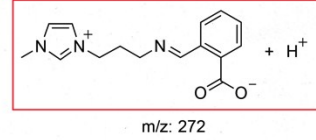
Positive mode
Before CO₂ bubbling

[Mass Spectrum]
Data : FAB-LR-2017-198 Date : 15-Feb-2018 08:57
Instrument : MStation
Sample : ZI
Note : No.210 Matrix:YOKUDEL
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 5.20 min Scan# : 27
BP : m/z 272 Int. : 693.65 (7273471)
Output m/z range : 50 to 601 Cut Level : 0.00 %

IL form



ZI form

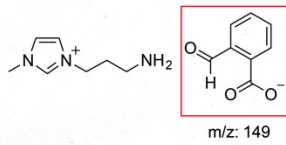


(b)

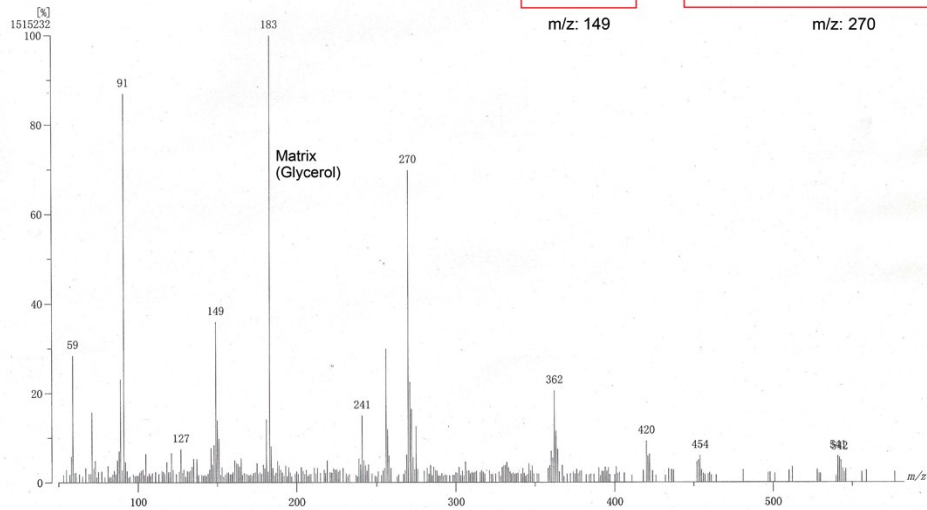
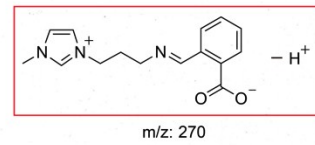
Negative mode
Before CO₂ bubbling

[Mass Spectrum]
Data : FAB-LR-2017-212 Date : 16-Feb-2018 11:29
Instrument : MStation
Sample : ZI
Note : No.210 Matrix:Glycerol
Inlet : Direct Ion Mode : FAB-
Spectrum Type : Normal Ion [MF-Linear]
RT : 6.40 min Scan# : 33
BP : m/z 183 Int. : 144.50 (1515232)
Output m/z range : 50 to 583 Cut Level : 0.00 %

IL form



ZI form



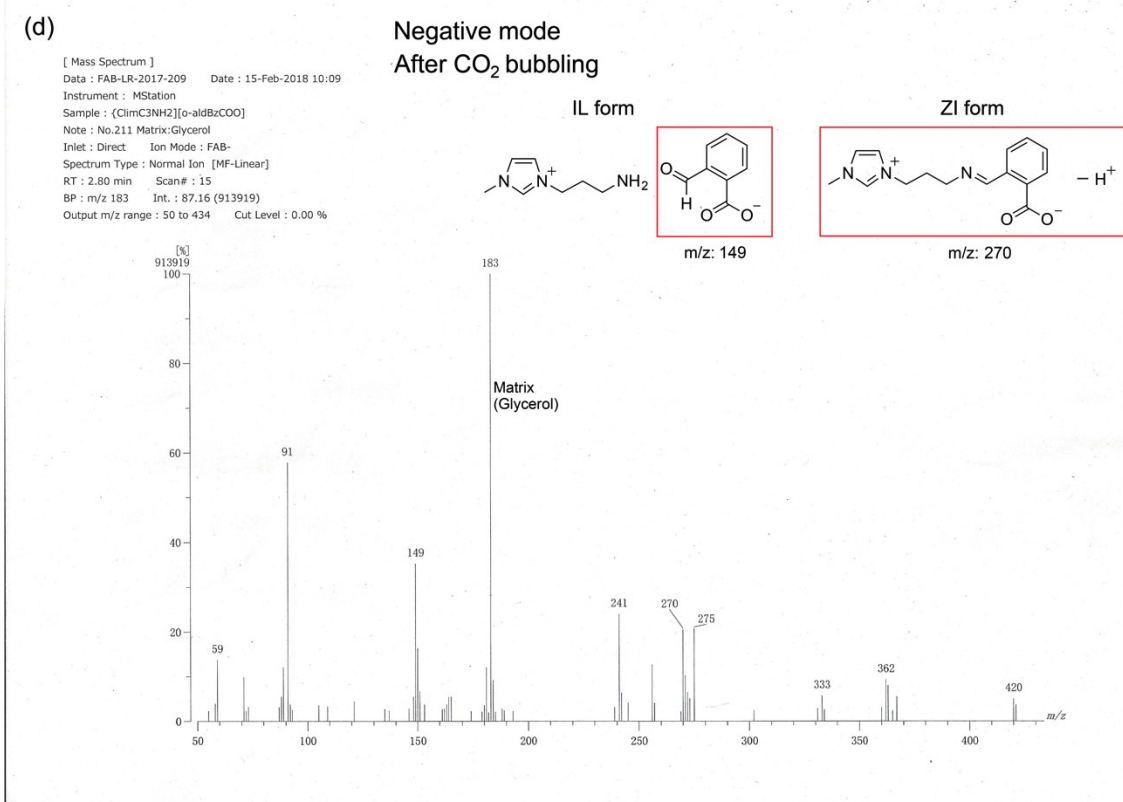
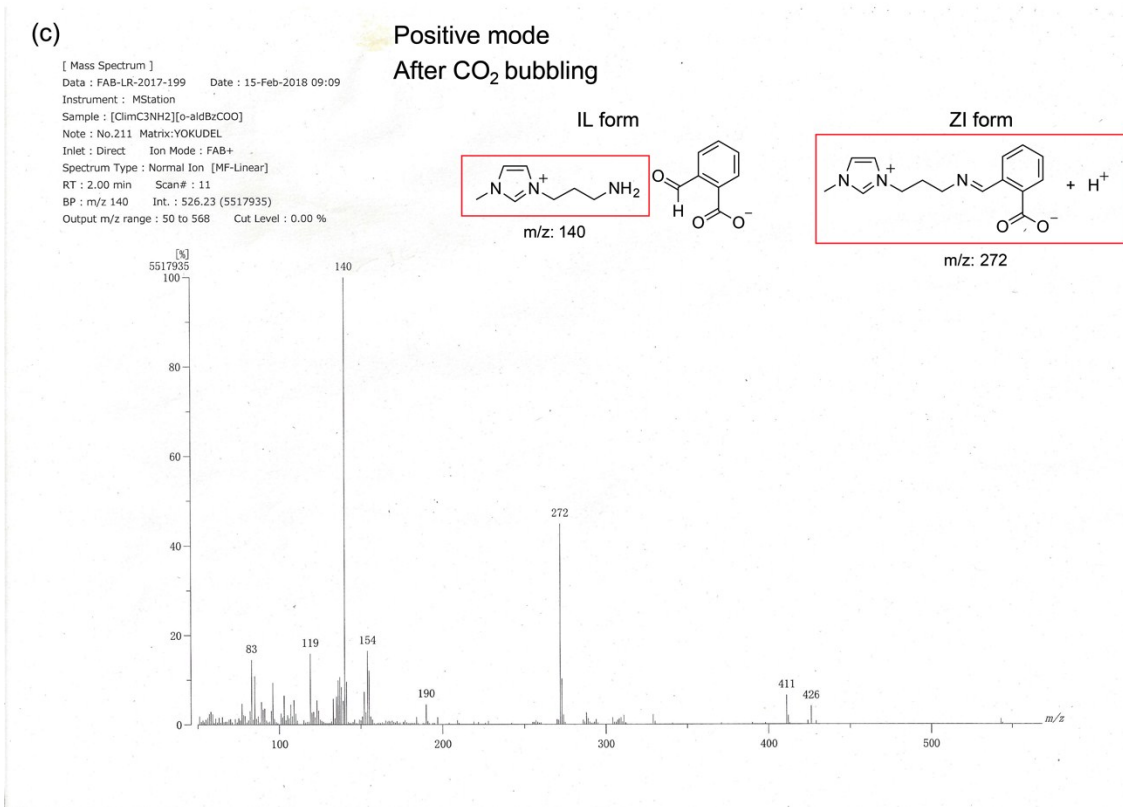


Fig. S3. Mass spectra (a, c: positive mode, and b, d: negative mode) of 1 wt% [C₃NH₂mim][o-aldBzCOO] aqueous solution (a, b) before and (c, d) after CO₂ bubbling.

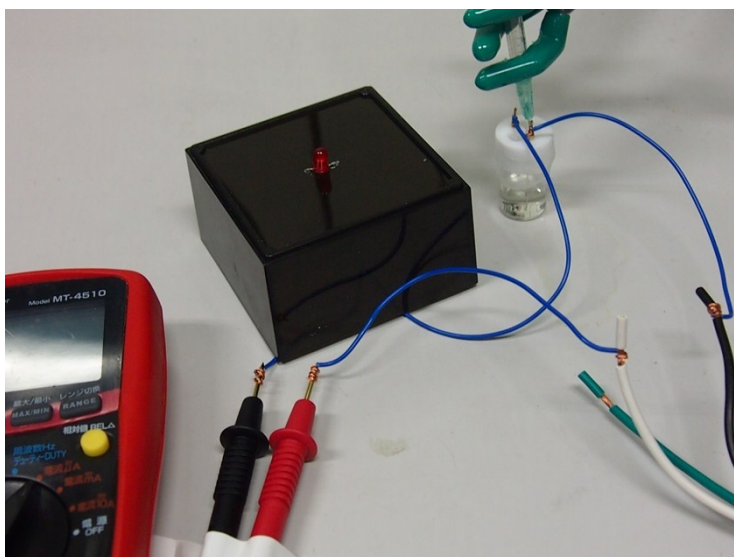


Fig. S4. A picture of the system for the emission experiment. The top right vial contains a $[\text{C}_3\text{NH}_2\text{mim}][o\text{-aldBzCOO}]$ solution. CO_2 and N_2 flowed from gas cylinders to the solution through the top right syringe. Nothing is inside the center box except for conducting wires (the box is used just for fixing the LED).