

## *Supplementary Information*

### **Synthesis of Zero-Valent Iron Nanoparticles by Laser Ablation in Formate Ionic Liquid under Atmospheric Conditions**

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## Experimental Procedures

### Materials

Cesium bicarbonate (> 95.0 %), 1-bromooctane (>95.0%), 2-propanol (>99.7%) and Fe<sub>2</sub>O<sub>3</sub> powder were purchased from Wako. Formic acid (>98%), ethanol (>99.5%), methanol (>99.0%), dichloromethane (>99.5%), and sodium bicarbonate (>99.6%) were purchased from Nacalai tesque. Sodium tetrafluoroborate (>98%) was purchased from Stera Chemifa. Trioctylphosphine (>95%) was purchased from Nippon Chemical Industrial Co Ltd. Lithium bis(trifluoromethylsulfonyl)imide (>99.8%) was purchased from Moritakagaku. Fe foil (>99%) was purchased from Niraco. Distilled water was produced from RFD240HA (ADVANTEC). All chemicals were used as received.

### Synthesis of cesium formate (CsHCOO)

Cesium bicarbonate (887 g, 2.72 mol) was dissolved into 800 mL of distilled water. Formic acid (350 g, 7.7 mol) was gradually added to the aqueous solution. In order to remove unreacted formic acid, the crude solution was evaporated under 2 kPa after adding 300 mL of distilled water. This process was conducted twice, and water was removed completely by evacuation under 1 Pa at 100 °C over 48 hours. Crude CsHCOO was recrystallized twice from ethanol. The resulted crystal of CsHCOO was dried under 1 Pa at 100 °C over 48 hours. CsHCOO was kept as the solution in 2-propanol at 0.30 mol kg<sup>-1</sup>.

### Synthesis of tetraoctylphosphonium tetrafluoroborate ([P<sub>8888</sub>]BF<sub>4</sub>)

1.2 equivalent 1-bromooctane (1108 g, 5.74 mol) was added to trioctylphosphine (1762 g, 4.75 mol) at 70 °C under nitrogen atmosphere and the reaction mixture was kept at 70 °C over 16 hours. The reaction mixture was cooled and used for the next reaction without further purification (the reaction yield was >99% by <sup>31</sup>P NMR (JEOL, JNM-ECA300)). [P<sub>8888</sub>]Br was dissolved in 1.5 L dichloromethane and 1.2 equivalent sodium tetrafluoroborate (625 g, 5.70 mol) was dissolved in 1.0 L distilled water, respectively. The aqueous solution of sodium tetrafluoroborate was filtrated to remove the impurities that did not dissolve into the water. After mixing the solution vigorously, the dichloromethane layer was separated and washed by distilled water. After separating the water layer, methanol was added to the dichloromethane layer. The mixture was evaporated again to remove dichloromethane in the solution. [P<sub>8888</sub>][BF<sub>4</sub>] was purified by recrystallizing 5 times from methanol at 0 °C until its cation purity over 99.5% (<sup>31</sup>P NMR). The amount of residual bromide was checked by the Mohr titration using methanol as solvent, and anion purity was over 99.9%.

### Synthesis of tetraoctylphosphonium formate ([P<sub>8888</sub>]HCOO)

[P<sub>8888</sub>]BF<sub>4</sub> (36 g, 63 mmol) was dissolved into 300 g of 2-propanol. 230 g of 0.30 mol kg<sup>-1</sup> CsHCOO/2-propanol solution was added to the solution, and the mixture was stirred vigorously over 16 hours. The solution was filtrated to remove cesium tetrafluoroborate (CsBF<sub>4</sub>). After the evaporating the

solvent 2-propanol, 30 ml of hexane and 10 ml of H<sub>2</sub>O was added to the residual. After the separating the water phase, the organic layer was washed by water 3 times. After evaporation, [P<sub>888</sub>]HCOO was obtained and dissolved in 2-propanol to store. The sample was dissolved into CDCl<sub>3</sub>, and the concentration was prepared to 0.1 mol dm<sup>-3</sup>. NMR assignment was conducted comparing with NMR spectra of tetrabutylphosphonium formate we have assigned already.<sup>1</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 8.9(s, 1H; HCOO), 2.5-2.4(m, 8H; CH<sub>2</sub>), 1.6-1.4(m, 16H; CH<sub>2</sub>), 1.4-1.2(m, 32H; CH<sub>2</sub>), 0.9 (t, 12H; CH<sub>3</sub>)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 168.1(s, 1C; HCOO), 31.7(s, 4C), 30.9(d, J(C,P)=15Hz, 4C), 29.0(s, 8C), 22.7(s, 4C), 21.9(d, J(C,P)=4Hz, 4C), 19.0(d, J(C,P)=50Hz, 4C), 14.0(s, 4C)

### Synthesis of tetraoctylphosphonium bis(trifluoromethylsulfonyl)imide ([P<sub>888</sub>]TFSI)

[P<sub>888</sub>][BF<sub>4</sub>] (52 g, 91 mmol) was dissolved into 100 ml of dichloromethane. Lithium bis(trifluoromethylsulfonyl)imide (26 g, 91 mmol) was dissolved into 100 ml of distilled water. The aqueous solution was poured into [P<sub>888</sub>]BF<sub>4</sub>/dichloromethane solution, and the mixture was stirred vigorously over 16 hours. After the separating the water layer, the same concentration of lithium bis(trifluoromethylsulfonyl)imide aqueous solution was added to the organic layer, and the mixture was stirred vigorously over 16 hours. After the separating the water layer, the organic layer was washed by 100 mL of distilled water twice. [P<sub>888</sub>]TFSI was obtained by evaporating the solvent.

### Cyclic voltammetry measurement

The redox potential of [P<sub>888</sub>]HCOO was measured with a potentiostat (HAB-151A, Hokuto denko). The redox potential of neat [P<sub>888</sub>]HCOO could not be measured because of its high viscosity. For this reason, we measured the redox potential of [P<sub>888</sub>]HCOO in acetonitrile (1 mol kg<sup>-1</sup>). Platinum disk working electrode and platinum coil counter electrode were used for the measurement. Ag/Ag<sup>+</sup> counter electrode was used as a reference electrode. The measurement was conducted under nitrogen atmosphere at 21.5 ± 2 °C. The initial voltage was set to -1.7 V, and the voltage was swept to -0.5 V. After reaching -0.5 V the potential was swept to -2.0 V. Two scan rates were tested (20 mV sec<sup>-1</sup> and 5 mV sec<sup>-1</sup>).

### Fe NPs synthesis by laser ablation in [P<sub>888</sub>]HCOO

Fe NPs synthesis by laser ablation was conducted in a handmade cell whose structure is shown in Fig. 1. The cell was made of polyetheretherketone (PEEK) to get resistance to chemicals. The inner volume of the cell was about 4 ml. Each side of the cell had a penetrated hole whose diameter is 10 mm, and the holes standing face to face were at the same height. The holes were covered by a quartz window (OPSQ-10C01-P, Optosigma), and used for the laser beam pathway. The stirring rod was made of polytetrafluoroethylene (PTFE). The stirring rod was connected to a gear motor (Tanosikousaku No. 198, Tamiya) and the rotation rate was controlled by a DC voltage (AD-8724D, AND).

As an ablation target, a 0.2 mm thickness of Fe foil was attached on the stirring rod. The target was set inside the cell filled with about 2.5 ml of  $[P_{888}]HCOO$ , which was dried under 1 Pa at  $60^{\circ}C$  before use. The target was irradiated by 532 nm laser pulses (20 mJ,  $5 \pm 2$  ns) from a Nd:YAG laser (Minilite, Continuum) at 5 Hz under atmosphere. Laser ablation was conducted for 120 minutes. After NPs preparation,  $^1H$  NMR of the sample solution containing Fe NPs was measured, and the water content of the solution was estimated from  $^1H$  NMR signal of water (see Fig. S1). To check the decomposition of the phosphonium cation by the basic anion ( $HCOO^-$ ), the amount of cation decomposition after ablation was checked by  $^{31}P$  NMR signal (see Fig. S2).

#### **Fe NPs synthesis by laser ablation Fe NPs in $[P_{888}]TFSI$**

About 2 mL of  $[P_{888}]TFSI$ , which was dried under 1 Pa at  $60^{\circ}C$  before use, was poured into a quartz cell with 1 cm optical path length. As in the case of  $[P_{888}]HCOO$ , a Fe target attached to the rotating rod was immersed into the cell, and the laser ablation was conducted similarly.

#### **Fe NPs synthesis by laser ablation in thin coated $[P_{888}]HCOO$**

An Fe foil was put onto the bottom of a vessel of 10 mL volume made of glass, and about 0.5 g  $[P_{888}]HCOO$  was poured into the vessel to cover the Fe foil. Then the vessel was laid down, and the ablation was conducted as shown in Fig. S1. The other conditions for the ablation were the same for Fe NPs synthesis by laser ablation in  $[P_{888}]HCOO$ .

#### **X-ray absorption spectrum**

Fe K-edge X-ray absorption measurements were conducted at BL-12C at Photon Factory of High Energy Accelerator Research Organization (KEK) in Japan. XANES spectra of Fe NPs dispersed in ILs were measured by the fluorescence mode using a MSSD element. The reference spectra (Fe foil and  $Fe_2O_3$  powder) were measured by a transmission mode. Baseline correction and normalization of the spectra were performed by Athena XAS data processing program (University of Chicago). The photon energy was calibrated with pre-edge peak of an Fe foil.

#### **TEM measurement**

Transmission electron microscopy (TEM) images were captured using a microscope JEM-3200FSK (JEOL). The images were acquired in an acceleration voltage 300 kV. For the specimen preparation in TEM, 20  $\mu$ L of  $[P_{888}]HCOO$  containing Fe NPs prepared by laser ablation was dissolved into 4 mL of methanol. The solution was dropped onto a grid covered by a holey amorphous carbon film, and dried at room temperature in a pressure around 1 Pa over 16 hours. Subsequently, the grid was exposed to atmosphere and inserted into the microscope.

## **STEM measurement**

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were captured using an aberration-corrected microscope JEM ARM200F (JEOL). The images were acquired in an acceleration voltage 200 kV. The sample used for the STEM measurement was the same as those used for the TEM measurement. EDS analysis was also conducted by this system.

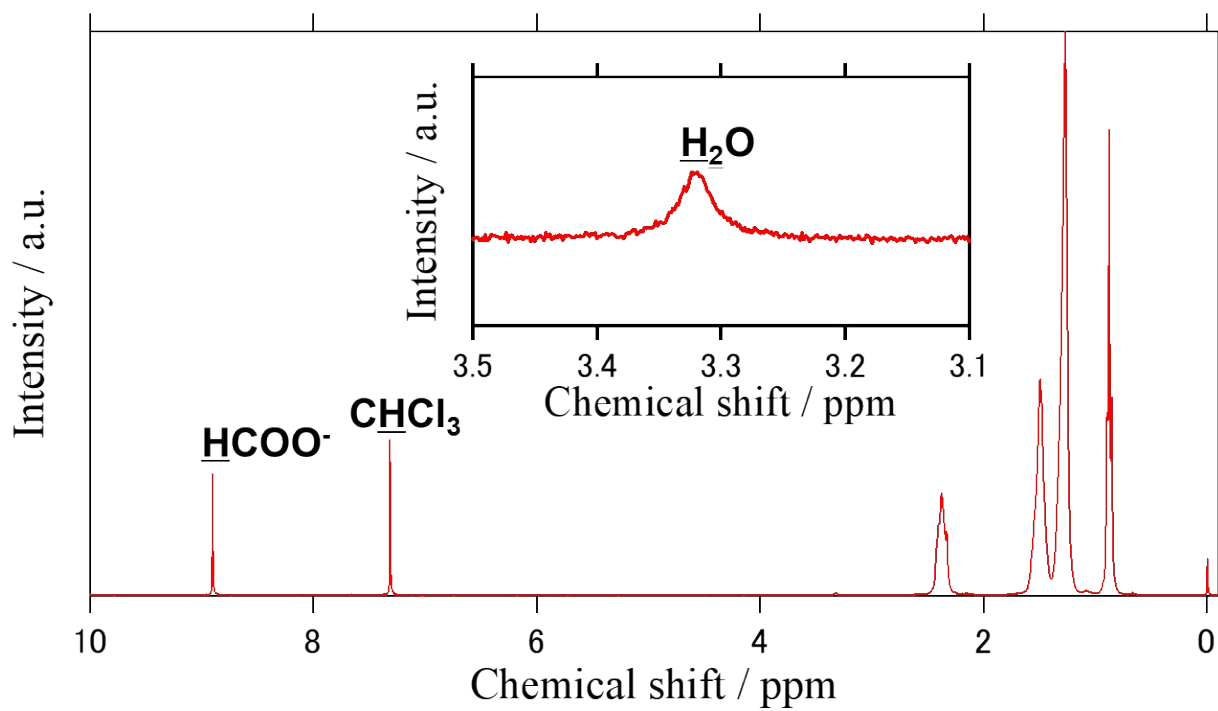


Fig. S1  $^1\text{H}$  NMR spectrum of  $[\text{P}_{888}]\text{HCOO}$  containing Fe NPs.

The water content was calculated by the integral ratio. 3 mol% water was contained in the colloidal solution.

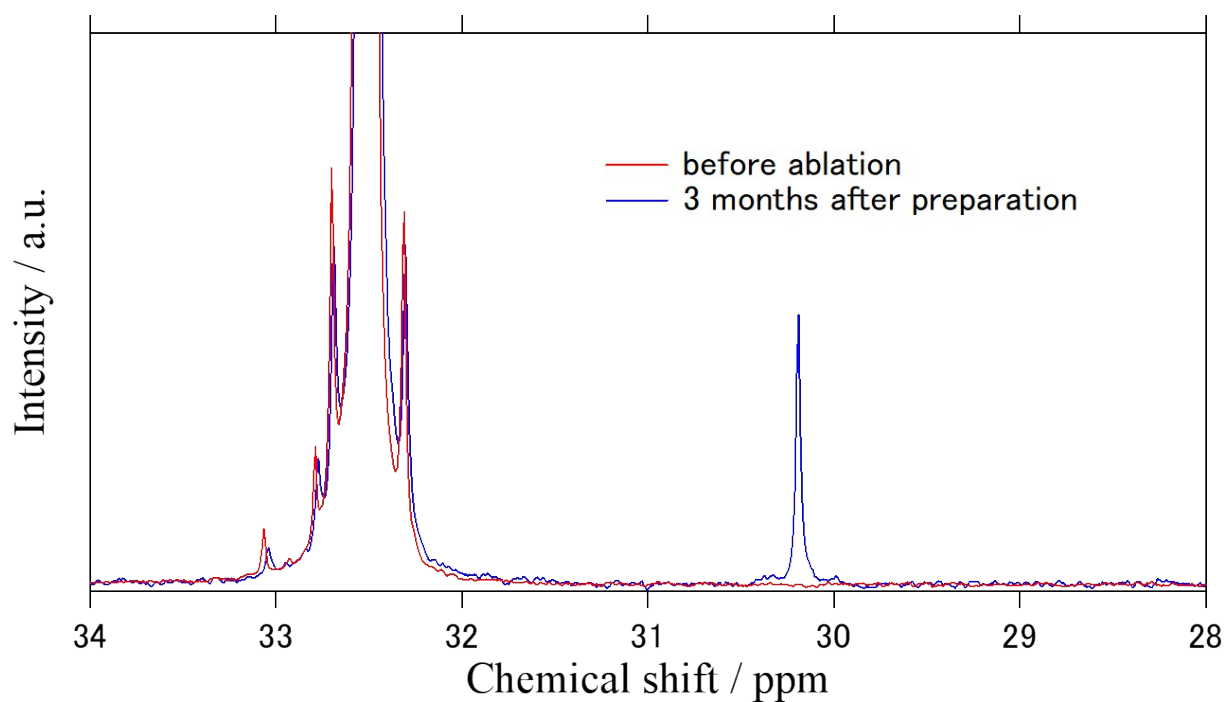


Fig. S2  $^{31}\text{P}$  NMR spectra of  $[\text{P}_{888}]\text{HCOO}$ .

The purity was calculated by the integral ratio. The cation purity was over 99.7% before ablation. The peaks at 33.2 ppm and 32.9 ppm were due to impurities which were not excluded by recrystallization. The peak at 30.2 ppm was due to impurity after the ablation experiment. The cation purity 3 month after ablation experiment was 98.2%.

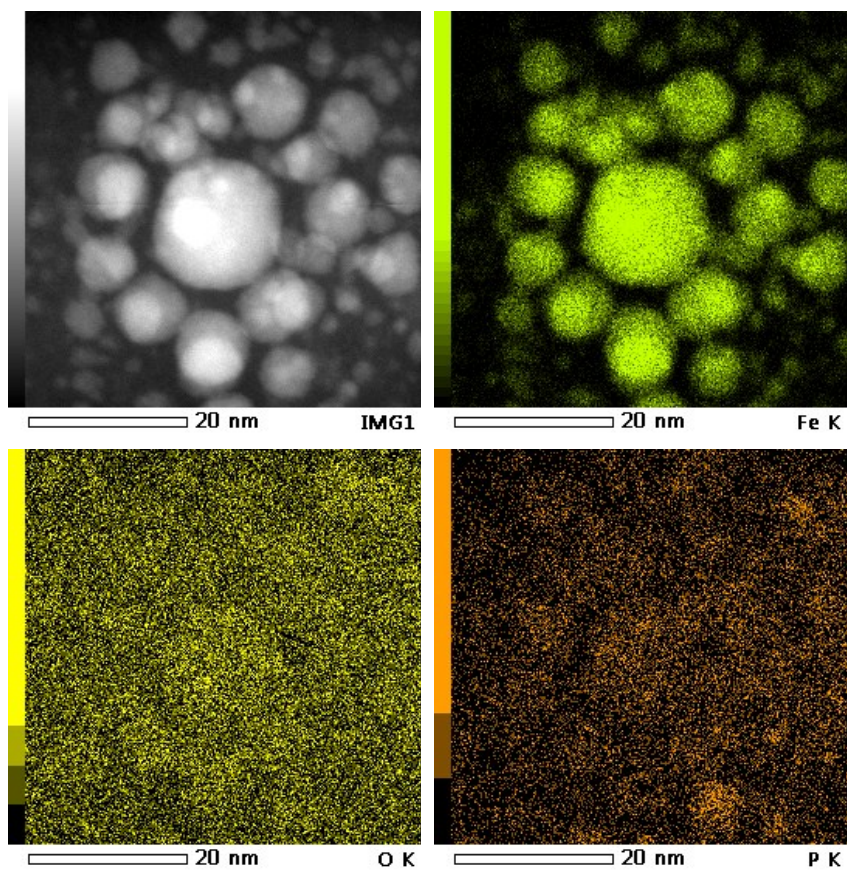


Fig. S3 HAADF-STEM image of Fe NPs produced by laser ablation (upper left), and element mapping of iron (upper right), oxygen (bottom left) and phosphorus (bottom right), conducted by EDS respectively.



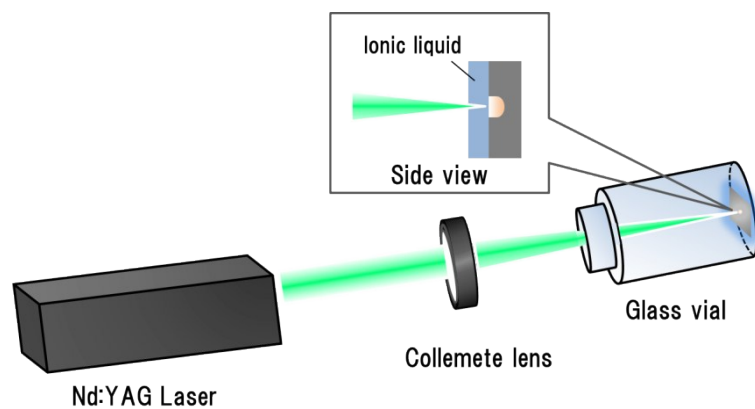


Fig. S4 Schematic illustration of laser ablation setup of side mode.

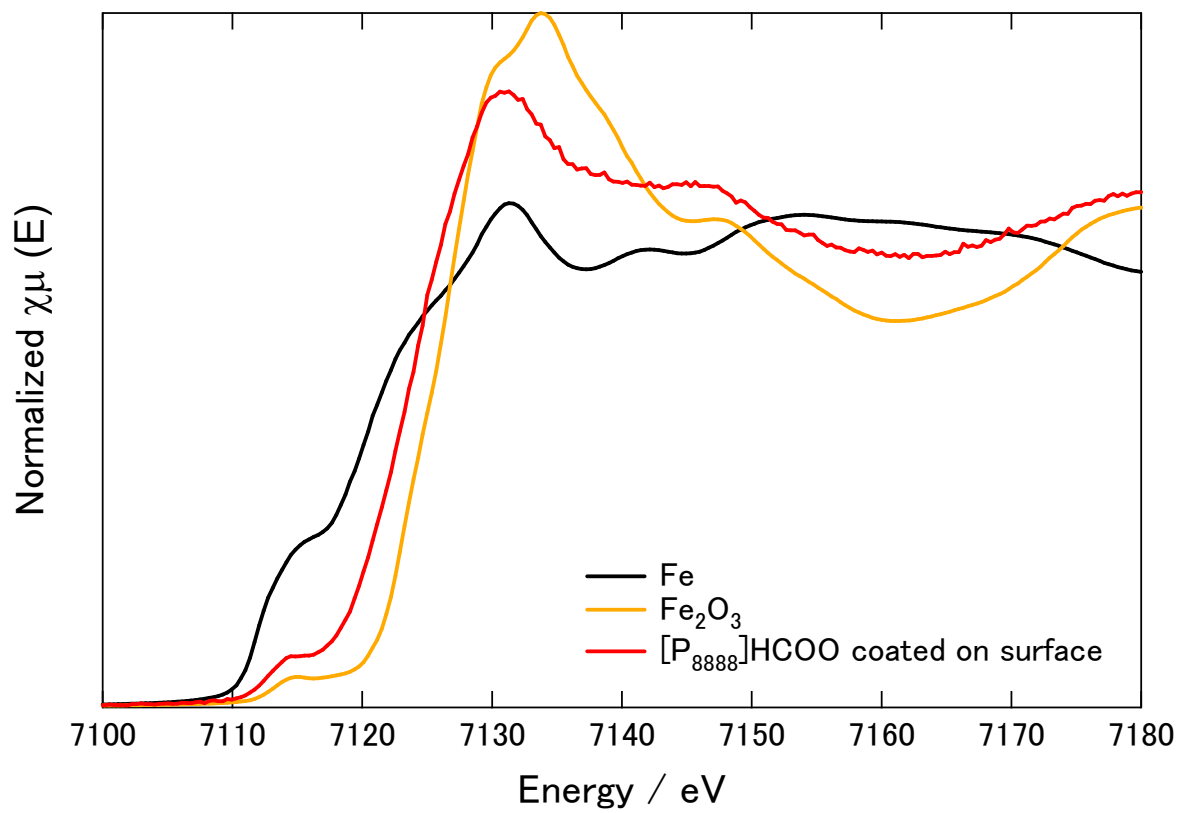


Fig. S5 XANES spectra of Fe NPs prepared in coated with  $[\text{P}_{888}]\text{HCOO}$  and references.

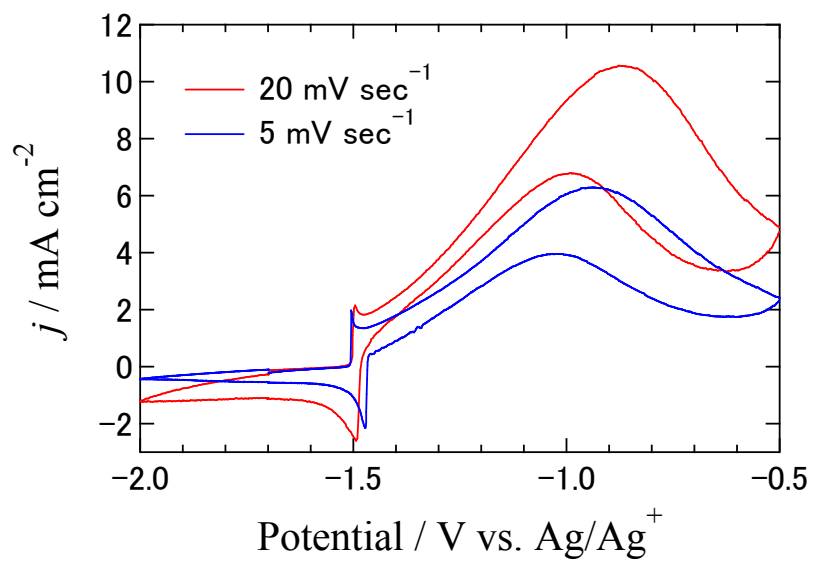


Fig. S6 Cyclic voltammograms of 1 mol  $\text{kg}^{-1}$   $[\text{P}_{888}]\text{HCOO}$  acetonitrile solution.

## References

- 1 Y. Yasaka, M. Ueno and Y. Kimura, *Chem. Lett.*, 2014, **43**, 626