

Supporting Information

Synthesis of pyrrolidinium-based plastic crystals exhibiting high ionic conductivity at ambient temperature

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Experimental

General. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker spectrometer at room temperature. The signals were referenced against tetramethylsilane as an internal standard. Mass spectra were obtained with a JMS-T100LC. Elemental analyses were carried out with a Perkin Elmer PE 2400-II. DSC measurements were performed on a DSC7020 (Hitachi High-Technologies) at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$. TG-DTA measurements were performed on a TG-DTA7200 (Hitachi High-Technologies) at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$ under a N_2 atmosphere. The XRD profiles were obtained over the 2θ range of 1.5 to 40° with a Rigaku SmartLab X-ray diffractometer operating at 45 kV and 200 mA using a Ni-filtered $\text{CuK}\alpha$ target. Ionic conductivity measurements were carried out by means of a stainless cell (TYS-00DM01, Toyo System Co., Ltd.). The samples were dissolved in super dehydrated dichloromethane. Glass paper (thickness (d); $50.0\text{ }\mu\text{m}$, porosity (ϕ); 0.930) was infiltrated with these solutions, and then the glass papers were dried *in vacuo* at $50\text{ }^\circ\text{C}$ for 2 days to completely remove the solvent. The glass papers were sandwiched between two platinum electrodes (area (S); 2.56 cm^2) that had been polished with 1.0 , 0.3 , and $0.05\text{ }\mu\text{m}$ Al_2O_3 powders. Ionic conductivities (σ) were measured using an VSP-300 (BioLogic) at a frequency range of 5 Hz - 1 MHz and

applied voltage of 10 mV and determined as follows.

$$\sigma = \left(\frac{d}{R \times S} \right) \times \frac{1}{\phi}$$

We used the porosity of the glass paper to correct the cell constant. The temperature was controlled using a constant temperature oven (SU262, Espec Corp.). Optimization of ion structures was performed using a molecular modeling software, Chem3D (Chem office). Ion radius of each ion was calculated using computational chemical software, winmostar (X-Ability).

Materials. Lithium bis(fluorosulfonyl)amide, lithium 1,1,2,2,3,3-hexafluoropropane-1,3-disulfoneamide, lithium nonafluorobutanesulfonate and lithium 1,1,2,2,2-pentafluoro-*N*-[(1,1,2,2,2-pentafluoroethyl)sulfonyl]amide were purchased from Kishida Chemical Co., Ltd. *N*-Methylpyrrolidine (97 % >) was purchased from Sigma-Aldrich Co. LLC. Sodium tricyanomethanide was purchased from Tokyo Chemical Industry CO., Ltd. Silver nitrate and Iodoethane (> 98.0%) were purchased from Wako Pure Chemical Industries, Ltd. All solvents were purchased from Kanto or Wako, and appropriately purified if necessary.

***N*-Ethyl-*N*-methylpyrrolidinium iodide ([C₂mpyr]I).** [C₂mpyr]I was synthesized via quaternization of *N*-methylpyrrolidine with iodoethane in acetonitrile. The mixture was stirred in ice water bath for 24 h. The product was reprecipitated by ethyl acetate, and then the precipitation was collected by filtration. The filtrate was dried under vacuum at 60 °C for 24 h (yields generally 80 to 90 %).

Silver tricyanomethanide (Ag[TCM]). Ag[TCM] was synthesized via anion exchange reaction by mixing of silver nitrate with sodium tricyanomethanide in water. The mixture was stirred at room temperature for 24 h. The product was washed by water, and then the white precipitation was collected by filtration. The filtrate was filtered dried under vacuum at 60 °C for 24 h (yields generally 90 to 95 %).

***N*-Ethyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)amide ([C₂mpyr][FSA]).** [C₂mpyr]I was dissolved in deionized water. Lithium bis(fluorosulfonyl)amide (LiFSA) (the mole number of LiFSA was 1.2 times larger than that of [C₂mpyr]I), which was dissolved in deionized water, was added dropwise to the aqueous solution. The mixture was stirred at room temperature for 1 h. The precipitated viscous liquid was dissolved in dichloromethane, and then the organic phase was washed several times with small volumes of deionized water. (The iodide content of the plastic crystal was determined by

an AgNO₃ test. AgI has a solubility of 0.03 mg L⁻¹ in water at 25 °C, hence the plastic crystal synthesized will have an iodide content below this value.) The solvent was removed by a rotary evaporator. Finally, the product was dried *in vacuo* at 45 °C for 24 h (yields generally 70 to 80 %). MS (FAB⁺): *m/z* 114.1 [M], 408.2 [2M+X]⁺, MS (FAB⁻): *m/z* 180.0 [X]⁻, 474.0 [M+2X]⁻. Anal. Calcd. For C₇H₁₆N₂O₄S₂F₂: C, 28.6; H, 5.48; N, 9.52; S, 21.8; found: C, 28.7; H, 5.32; N, 9.50; S, 21.9.

***N*-Ethyl-*N*-methylpyrrolidinium tricyanomethanide ([C₂mpyr][TCM]).** [C₂mpyr]I was dissolved in ethanol. Silver tricyanomethanide (AgTCM) was added to the ethanol solution. The mixture was stirred at 40 °C for 24 h. The by-product was filtered off and the ethanol in the filtrate was removed by a rotary evaporator. Finally, the product was dried *in vacuo* at 45 °C for 24 h (yields generally 70 to 80 %). MS (FAB⁺): *m/z* 114.1 [M], 318.3 [2M+X]⁺, MS (FAB⁻): *m/z* 90.0 [X]⁻, 294.1 [M+2X]⁻. Anal. Calcd. For C₁₁H₁₆N₄: C, 64.7; H, 7.89; N, 27.4; found: C, 64.5; H, 7.67; N, 27.4.

***N*-Ethyl-*N*-methylpyrrolidinium 1,1,2,2,2-pentafluoro-*N*-[(1,1,2,2,2-pentafluoroethyl)sulfonyl]amide ([C₂mpyr][BETA]).** [C₂mpyr]I was dissolved in deionized water. Lithium 1,1,2,2,2-pentafluoro-*N*-[(1,1,2,2,2-pentafluoroethyl)sulfonyl]amide (LiBETA), which was dissolved in deionized water, was added dropwise to the aqueous solution. The mixture was stirred at room temperature for 1 h. The precipitated viscous liquid was dissolved in dichloromethane, and then the organic phase was washed several times with small volumes of deionized water. (The iodide content of the plastic crystal was determined by an AgNO₃ test. AgI has a solubility of 0.03 mg L⁻¹ in water at 25 °C, hence the plastic crystal synthesized will have an iodide content below this value.) The solvent was removed by a rotary evaporator. Finally, the product was dried *in vacuo* at 45 °C for 24 h (yields generally 80 to 90 %). MS (FAB⁺): *m/z* 114.1 [M], MS (FAB⁻): *m/z* 380.1 [X]⁻. Anal. Calcd. For C₁₁H₁₆N₂O₄S₂F₁₀: C, 26.7; H, 3.26; N, 5.67; S, 13.0; found: C, 27.0; H, 3.18; N, 5.80; S, 12.9.

***N*-Ethyl-*N*-methylpyrrolidinium 1,1,2,2,3,3-hexafluoro propane-1,3-disulfoneamide ([C₂mpyr][CFSA]).** [C₂mpyr]I was dissolved in deionized water. Lithium 1,1,2,2,3,3-hexafluoro propane-1,3-disulfoneamide (LiCFSA) (the mole number of LiCFSA was 1.2 times larger than that of [C₂mpyr]I), which was dissolved in deionized water, was added dropwise to the aqueous solution. The mixture was stirred at room temperature for 1 h. The precipitated viscous liquid was dissolved in dichloromethane, and then the organic

phase was washed several times with small volumes of deionized water. (The iodide content of the plastic crystal was determined by an AgNO_3 test. AgI has a solubility of 0.03 mg L^{-1} in water at $25 \text{ }^\circ\text{C}$, hence the plastic crystal synthesized will have an iodide content below this value.) The solvent was removed by a rotary evaporator. Finally, the product was dried *in vacuo* at $45 \text{ }^\circ\text{C}$ for 24 h (yields generally 70 to 80 %). MS (FAB⁺): m/z 114.1 [M], 520.2 [2M+X]⁺, MS (FAB⁻): m/z 292.0 [X]⁻, 698.0 [M+2X]⁻. Anal. Calcd. For $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_4\text{S}_2\text{F}_6$: C, 29.6; H, 3.97; N, 6.89; S, 15.8; found: C, 29.5; H, 3.96; N, 6.87; S, 15.9.

***N*-Ethyl-*N*-methylpyrrolidinium nonafluorobutanesulfonate ([C₂mpyr][NFS]).**

[C₂mpyr]I was dissolved in deionized water. Lithium nonafluorobutanesulfonate (LiNFS) (the mole number of LiNFS was 1.2 times larger than that of [C₂mpyr]I), which was dissolved in deionized water, was added dropwise to the aqueous solution. The mixture was stirred at room temperature for 1 h. The precipitated viscous liquid was dissolved in dichloromethane, and then the organic phase was washed several times with small volumes of deionized water. (The iodide content of the plastic crystal was determined by an AgNO_3 test. AgI has a solubility of 0.03 mg L^{-1} in water at $25 \text{ }^\circ\text{C}$, hence the plastic crystal synthesized will have an iodide content below this value.) The solvent was removed by a rotary evaporator. Finally, the product was dried *in vacuo* at $45 \text{ }^\circ\text{C}$ for 24 h (yields generally 45 to 55 %). MS (FAB⁺): m/z 114.1 [M], 527.3 [2M+X]⁺, MS (FAB⁻): m/z 299.0 [X]⁻, 712.0 [M+2X]⁻. Anal. Calcd. For $\text{C}_{11}\text{H}_{16}\text{NO}_3\text{SF}_9$: C, 32.0; H, 3.90; N, 3.39; S, 7.76; found: C, 31.9; H, 3.73; N, 3.33; S, 7.73.

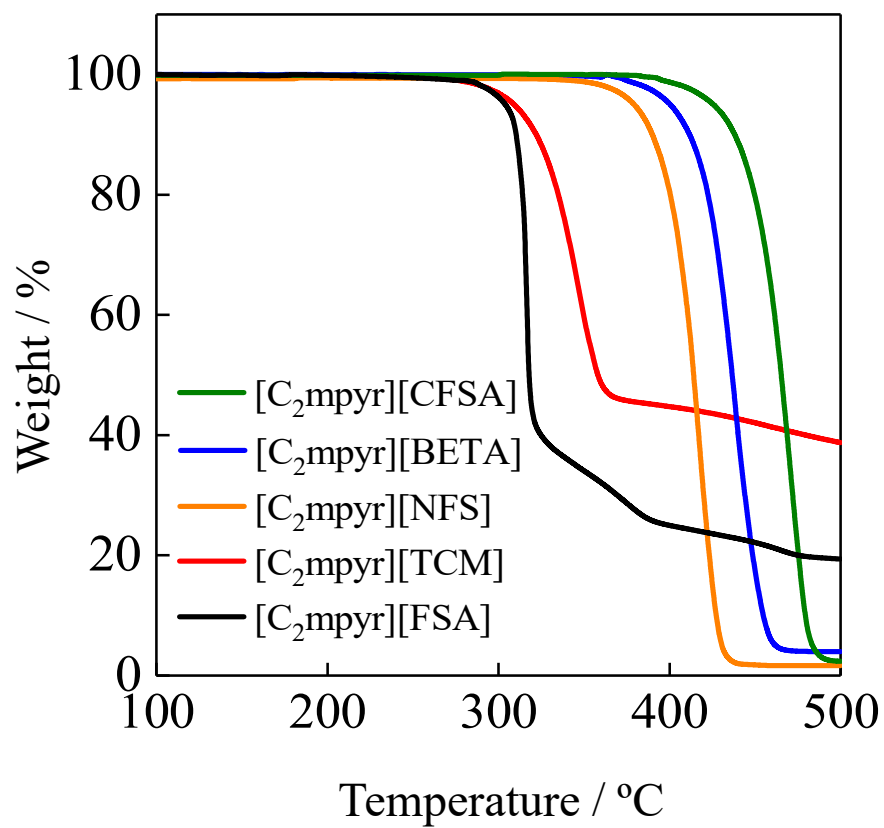


Fig. S1 TGA traces of [C₂mpyr]-based salts with various anion species.

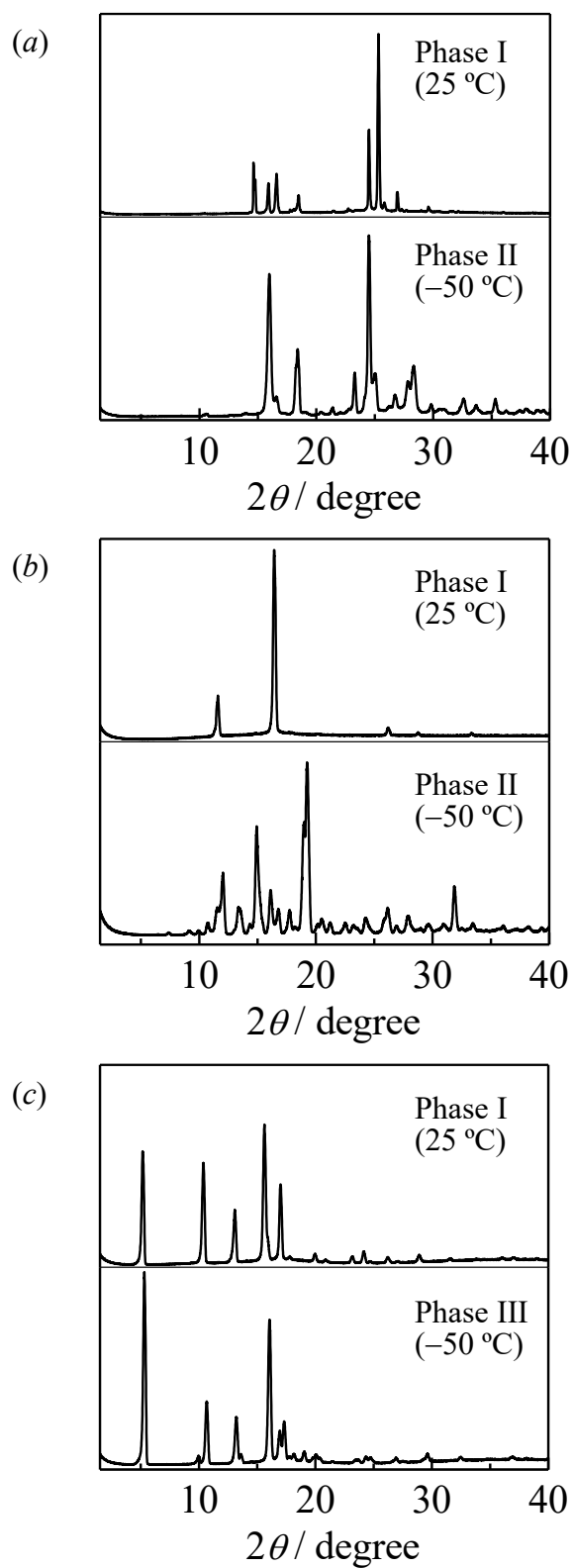
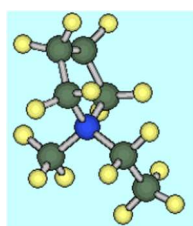
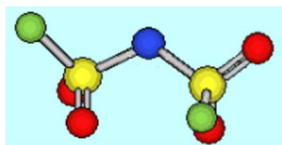


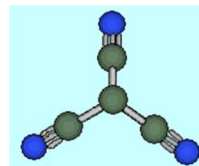
Fig. S2 XRD patterns of (a) [C₂mpyr][TCM], (b) [C₂mpyr][CFSA], and (c) [C₂mpyr][NFS].



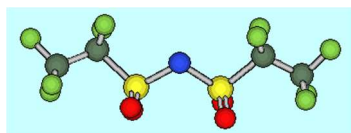
[C₂mpyr]⁺



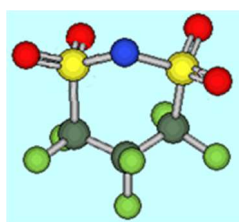
[FSA]⁻



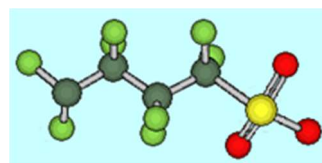
[TCM]⁻



[BETA]⁻



[CFSA]⁻



[NFS]⁻

Fig. S3 Optimised structures of [C₂mpyr]-based salts with various anion species.