Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Improved Ionic Conductivity for Amide-contained Electrolytes by Tuning Intermolecular Interaction: Effect of Branched Side-chains with Cyanoethoxy Groups

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Monomer synthesis

The monomer of poly(3-ethyl-3-cyanoethoxymethyloxetaneamide) (P3CEOA), 3-ethyl-3-cyanoethoxymethyloxetaneamide (3CEOA) was synthesized through the condensation reaction of 3-ethyl-3-cyanoethoxymethyloxetanecarbonyl (EOC) and 3,3'-((2-amino-2-((2-cyanoethoxy)methyl)propane-1,3-diyl)bis(oxy))dipropanenitrile (3CE) by following procedure.

Jones reagent was prepared by mixing chromium oxide VI (Wako Pure Chemical Co., 53.45 g), sulfuric acid (Sigma-Aldrich Co. LLC, 46 mL) and water (so as total volume to 200 mL). 3-ethyl-3oxetanemethanol (EHO, Tokyo Chemical Industry Co., Ltd, 24.84 g) acetone solution was added dropwise over a period of 30 min to Jones reagent (200 mL) dissolved in acetone (Wako Pure Chemical Co., 700 mL), subsequently stirred at 0°C for 2 h. The reaction mixture was quenched by adding isopropyl alcohol (Wako Pure Chemical Co.). After extracting the solution with dichloromethane (Wako Pure Chemical Co.) and water, volatile dichloromethane was removed using a rotary evaporator. The EOC was obtained by distilling the residue under reduced pressure (160°C, 0.02 mmHg), Yield: 40 %.

^{1}H NMR (δ, ppm from trimethylsilane (TMS) in $CDCl_3$): 0.89 (t, 3H, $–CH_2C\underline{H}_3$), 2.02 (q, 2H, $–C\underline{H}_2CH_3$), 4.44, 4.90 (dd, 4H, $–C\underline{H}_2–O–C\underline{H}_2–$) 9.09 (s, 1H, $–COO\underline{H}$)

40 wt% KOH (Wako Pure Chemical Co.) aqueous solution, tris(hydroxymethyl) aminomethane (THAM, Tokyo Chemical Industry Co., Ltd, 12.2 g), dioxane (Wako Pure Chemical Co., 100 mL) and acrylonitrile (Wako Pure Chemical Co., 39.3 mL) was mixed and stirred for 24 h at room temperature, then the solution was neutralized with 1 M HCl (Wako Pure Chemical Co., 100 mL). After extracting the solution with dichloromethane and water, volatile dichloromethane was removed using a rotary evaporator, subsequently purified via column chromatography (methanol (Wako Pure Chemical Co.): ethyl acetate (Wako Pure Chemical Co.) = 1: 4). Yield: 31%

^{1}H NMR (δ, ppm from trimethylsilane (TMS) in $CDCl_3$): 2.62 (t, 2H, $–C\underline{H}_2CN$), 3.46 (s, 2H, $C–C\underline{H}_2–O$), 3.70 (t, 2H, $–C\underline{H}_2CH_2CN$)

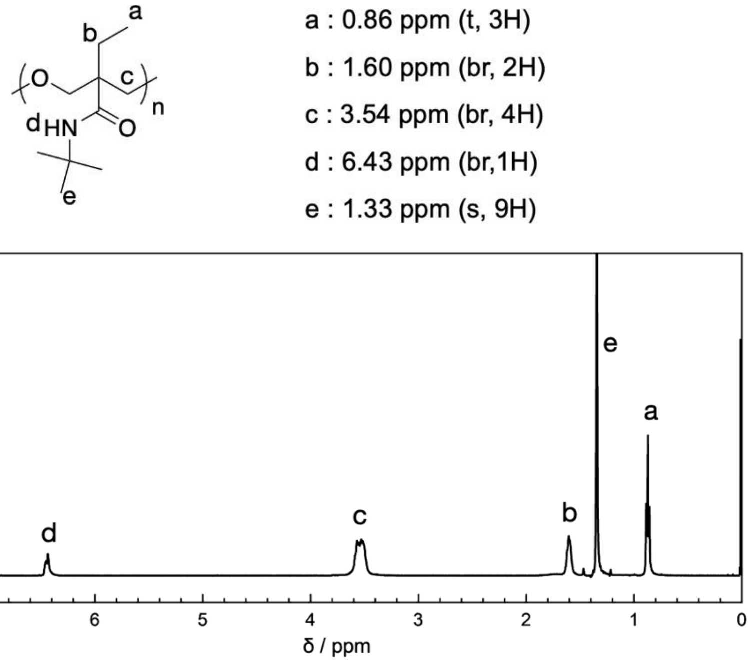
3CEOA was synthesized by following procedure. EOC (6.72 g), 3CE (14.46 g), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, Tokyo Chemical Industry Co., Ltd, 11.87 g), and 4-dimethylaminopyridine (DMAP, Wako Pure Chemical Co., 25.90 g) was dissolved into dichloromethane (250 mL), subsequently stirred at room temperature for 24 h. After condensation reaction, the solution was neutralized with 1 M HCl (100 mL) then washed with saturated $NaHCO_3$ (Wako Pure Chemical Co.) aqueous solution. Remained dichloromethane was removed with a rotary evaporator. The obtained solution was purified via re-crystallization. Yield: 58 %

^{1}H NMR (δ, ppm from trimethylsilane (TMS) in $CDCl_3$): 0.93 (t, 3H, $–CH_2C\underline{H}_3$), 2.02 (q, 2H, $–C\underline{H}_2CH_3$), 2.61 (t, 6H, $–CH_2C\underline{H}_2CN$), 3.70 (t, 6H, $–C\underline{H}_2CH_2CN$), 3.88 (s, 6H, $C–C\underline{H}_2–O$), 4.43, 4.84 (dd, 4H, $–C\underline{H}_2–O–C\underline{H}_2–$)

The monomer of poly(3-ethyl-3-*tert*-butyloxetaneamide) (PtBuOA), 3-ethyl-3-*tert*-butyloxetaneamide (tBuOA) was synthesized through the condensation reaction of EOC and *tert*-butylamine (Tokyo Chemical Industry Co., Ltd).

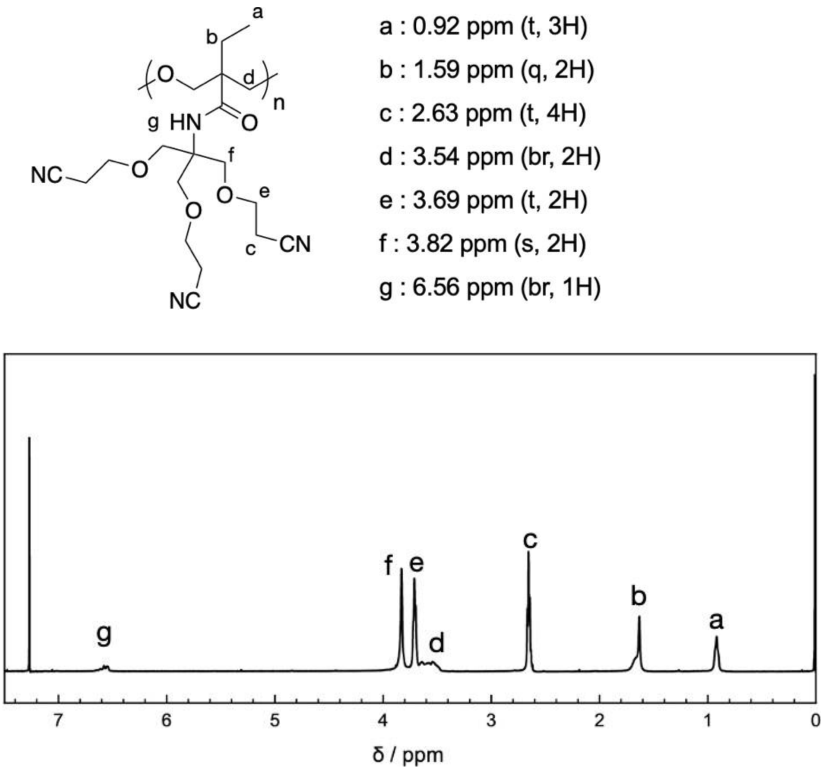
ECO (8.07 g), *tert*-butylamine (6.91 g), EDC·HCl (15.45 g), and DMAP (3.28 g) was dissolved into dichloromethane (200 mL), then stirred at room temperature for 24 h. The solution was neutralized and purified following the same procedure as 3CEOA. Yield: 51 %

^{1}H NMR (δ, ppm from trimethylsilane (TMS) in $CDCl_3$): 0.91 (t, 3H, $–CH_2C\underline{H}_3$), 1.38 (s, 9H, $–C–(C\underline{H}_3)_3$), 1.99 (q, 2H, $–C\underline{H}_2CH_3$), 4.40, 4.83 (dd, 4H, $–C\underline{H}_2–O–C\underline{H}_2–$), 5.21 (s, 1H, $–N\underline{H}$)



a : 0.86 ppm (t, 3H)
b : 1.60 ppm (br, 2H)
c : 3.54 ppm (br, 4H)
d : 6.43 ppm (br,1H)
e : 1.33 ppm (s, 9H)

Figure S1 ^{1}H NMR spectra of PtBuOA in deuterated dichloromethane.



a : 0.92 ppm (t, 3H)
b : 1.59 ppm (q, 2H)
c : 2.63 ppm (t, 4H)
d : 3.54 ppm (br, 2H)
e : 3.69 ppm (t, 2H)
f : 3.82 ppm (s, 2H)
g : 6.56 ppm (br, 1H)

Figure S2 ^{1}H NMR spectra of P3CEOA in deuterated dichloromethane.

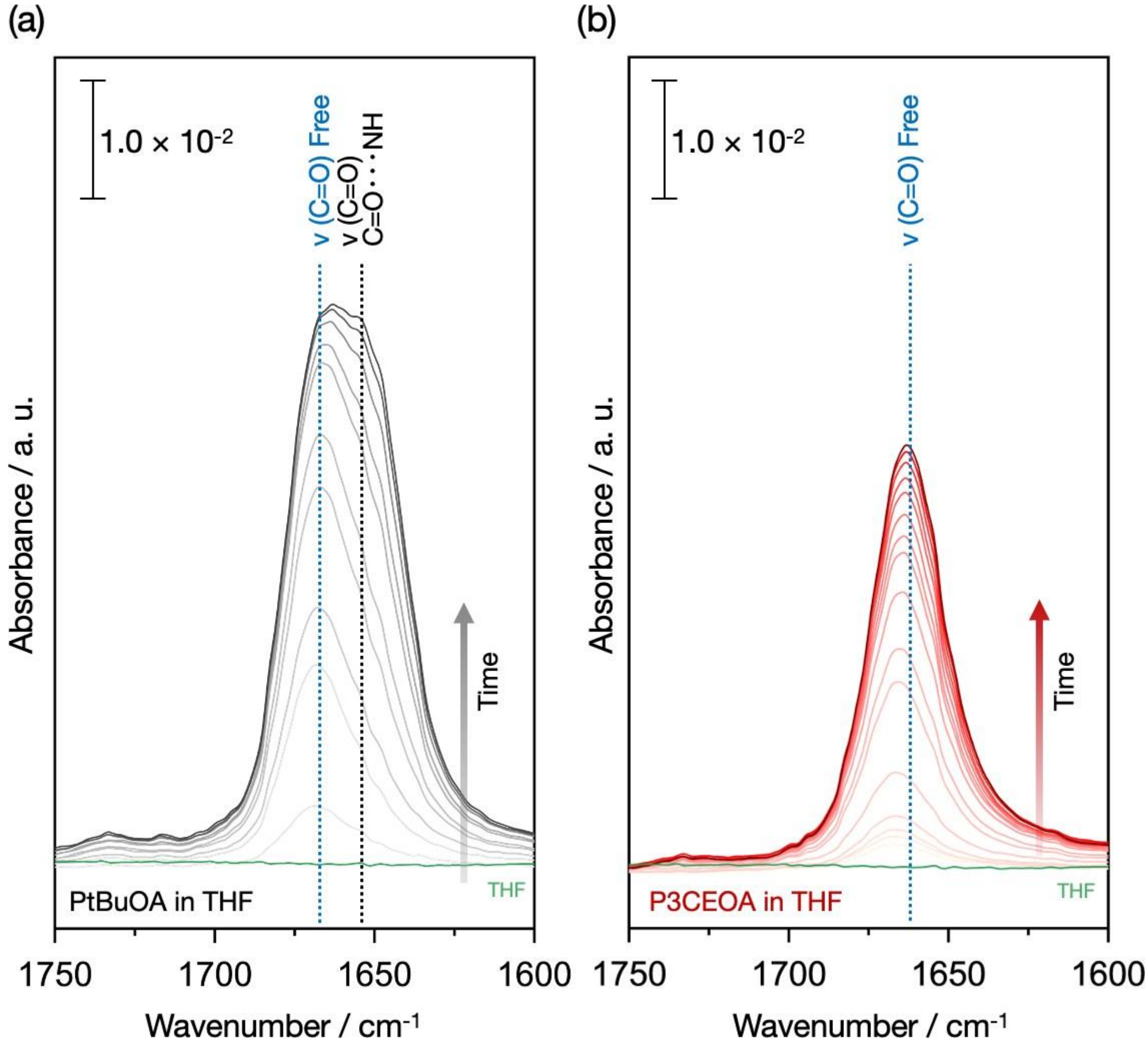
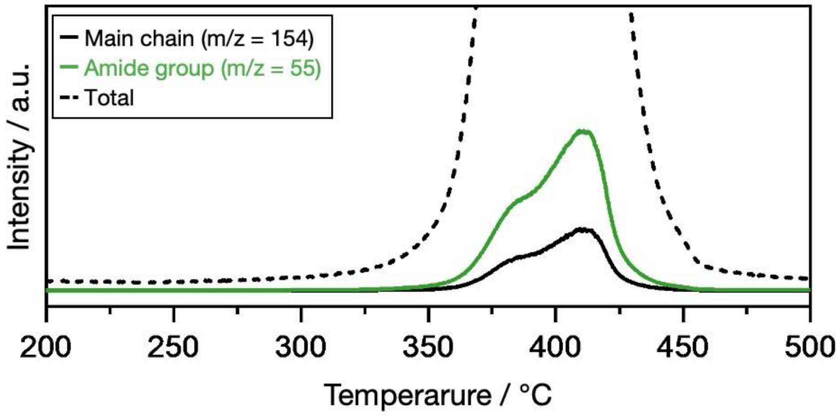


Figure S3 Infrared (IR) spectra of C=O stretching for (a) PtBuOA and (b) P3CEOA where the polymer dissolved into THF at room temperature. Each polymer was first completely dissolved into THF (bottom peak), then dried for 1 h under ambient pressure during IR measurement (in order from the bottom to top). IR spectra for THF (green line) is also shown for comparison.

(a) PtBuOA



(b) PtBuOA$_{16}$LiTFSA

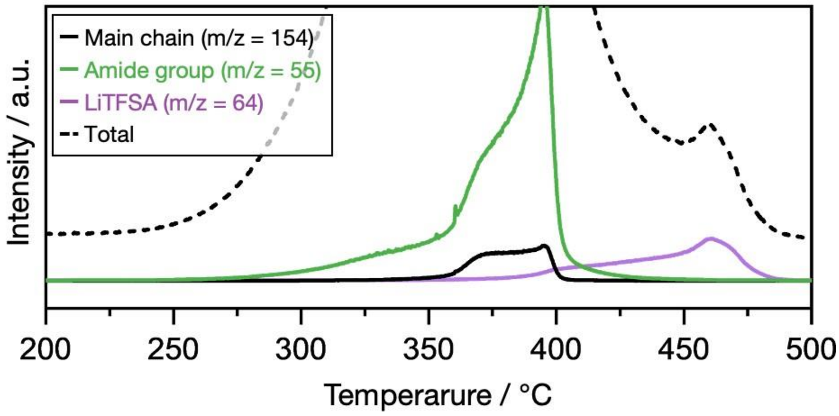
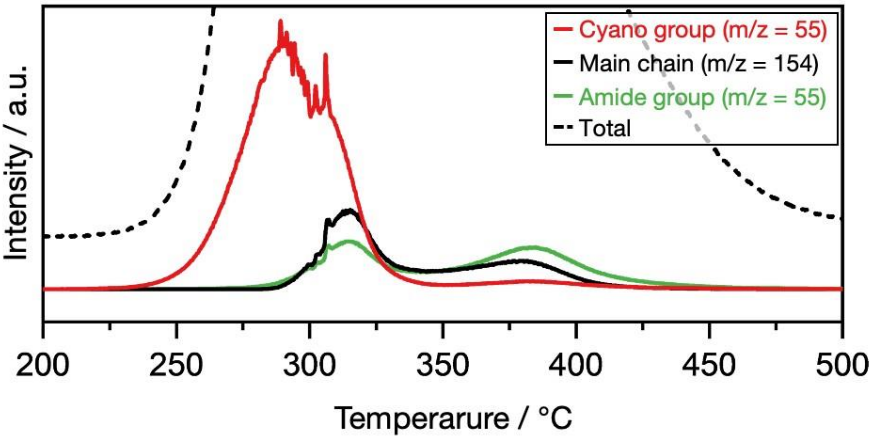


Figure S4 Gas chromatography–mass spectrometry (GC-MS) analysis for pristine (a) PtBuOA and (b) PtBuOA$_{16}$LiTFSA electrolytes. GC-MS curve was obtained by heating from 100°C to 500°C at a heating rate of 20°C min^{-1} under air. A gas chromatography–mass spectrometry (GC-MS) spectra were obtained by a gas chromatograph−mass spectrometer (GCMS-QP2010 Ultra, Shimadzu). A small amount of polymer electrolytes (~5 mg) was put in an aluminum pan. The samples were then pre-heated to 150 °C and held for 10 min to remove the residual water.

(a) P3CEOA



(b) P3CEOA$_{16}$LiTFSA

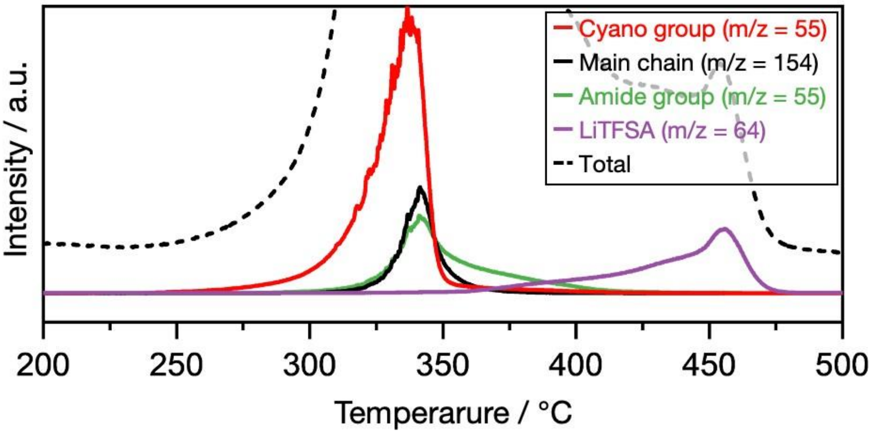
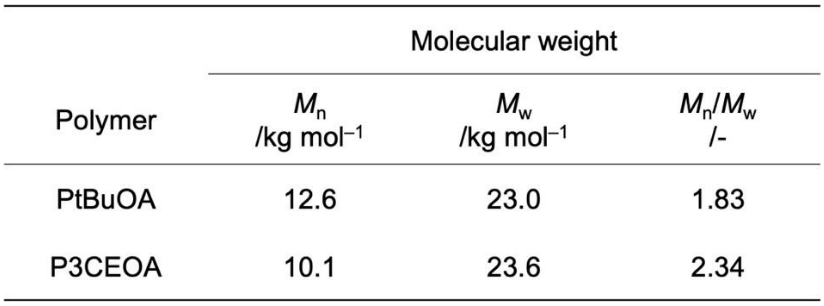


Figure S5 Gas chromatography–mass spectrometry (GC-MS) analysis for pristine (a) P3CEOA and (b) P3CEOA$_{16}$LiTFSA. GC-MS curve was obtained by heating from 100°C to 500°C at a heating rate of 20°C min^{-1} under air. A gas chromatography–mass spectrometry (GC-MS) spectra were obtained by a gas chromatograph−mass spectrometer (GCMS-QP2010 Ultra, Shimadzu). A small amount of polymer electrolytes (∼5 mg) was put in an aluminum pan. The samples were then pre-heated to 150 °C and held for 10 min to remove the residual water.

Table S1 Molecular weights (M_n and M_w) and polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) of PtBuOA and P3CEOA.



Polymer	Molecular weight		
	M_n /kg mol^{-1}	M_w /kg mol^{-1}	M_n/M_w /-
PtBuOA	12.6	23.0	1.83
P3CEOA	10.1	23.6	2.34

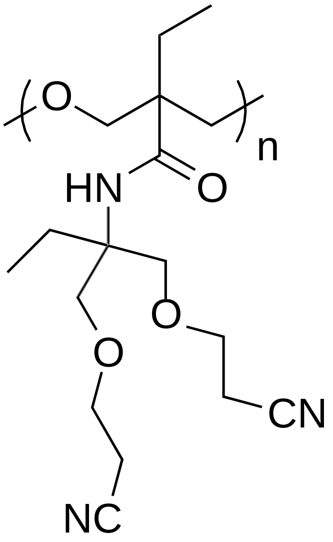


Figure S6 Molecular structure of P2CEOA having two cyanoethoxy group.

Table S2 The T_g value of PtBuOA*x*LiTFSA, P2CEOA*x*LiTFSA and P3CEOA*x*LiTFSA (x = 64–0.8).

x	T_g /°C		
	PtBuOA	P2CEOA	P3CEOA
(pure)	48.4	0.2	9.4
x = 64	31.2	-	-
x = 32	26.2	–0.4	–15.9
x = 16	40.6	–15.8	–17.5
x = 8	71.0	–12.9	–20.9
x = 2.4	-	–24.6	–24.4
x = 0.8	-	-	2.3

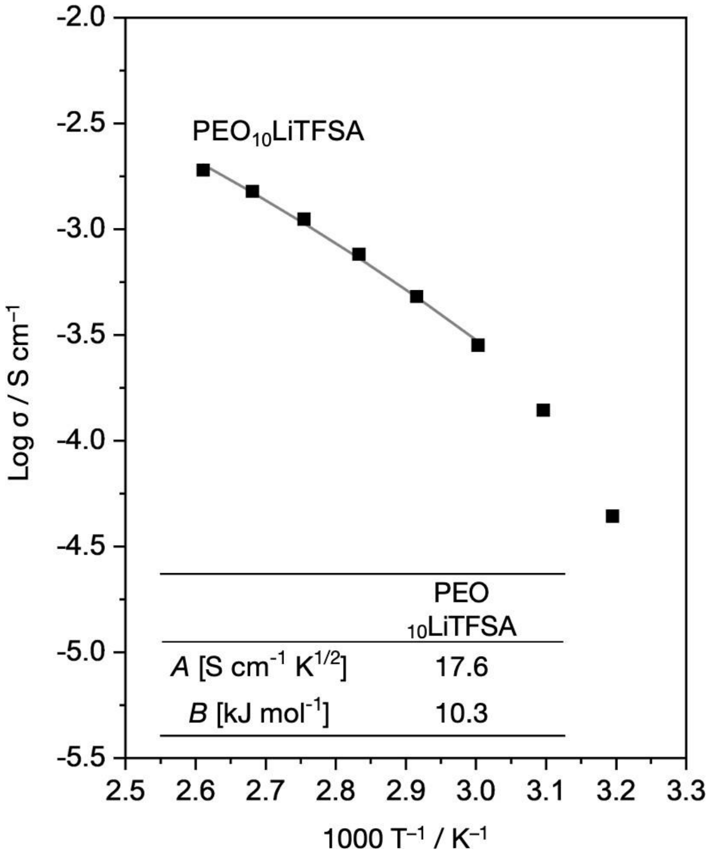


Figure S7 Arrhenius plots of the ionic conductivity for PEO$_{10}$LiTFSA. The electrochemical impedance spectroscopy was performed at 10 – 110°C. The solid line represents the Vogel-Tammann-Fulcher (VTF) fitting curves and the fitting parameters (*A* and *B*) for PEO$_{10}$LiTFSA were shown in the inset.

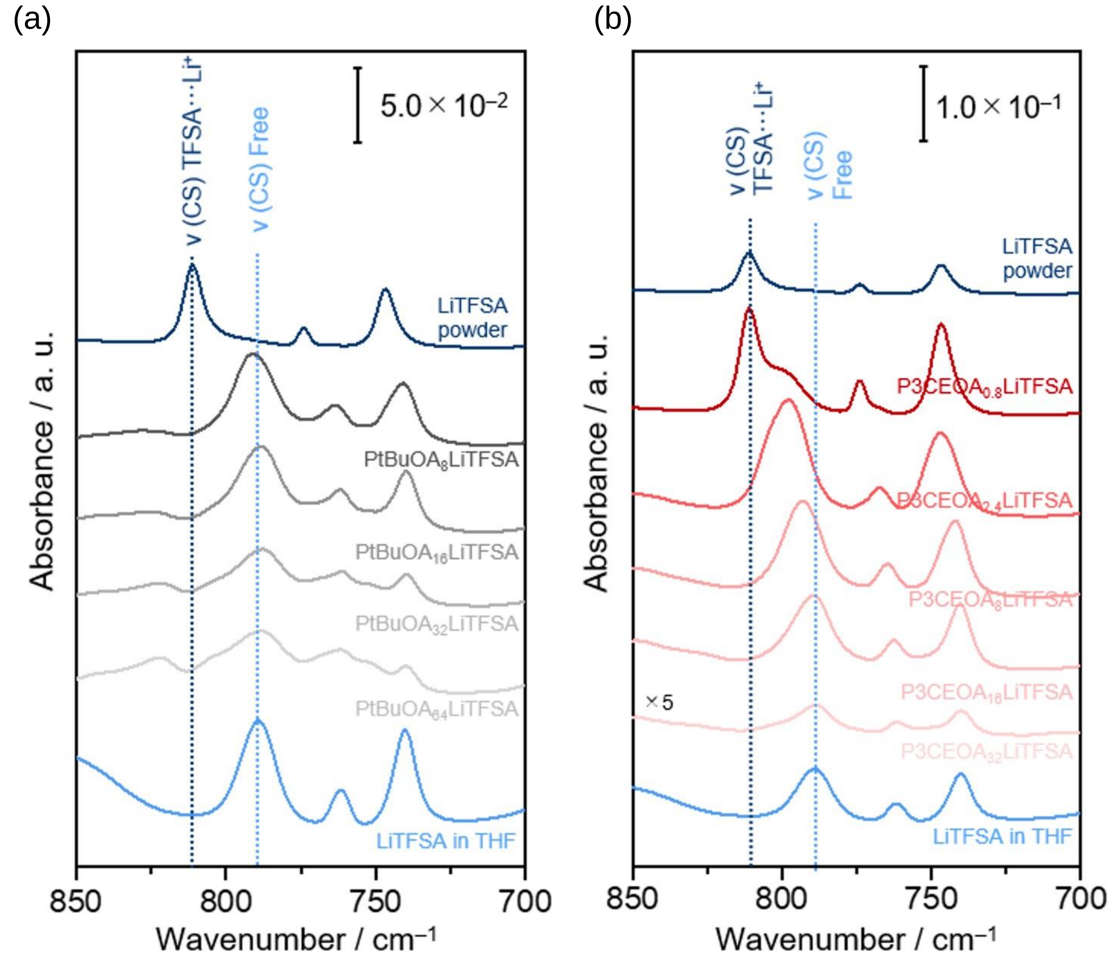


Figure S8 Infrared (IR) spectra and typical curve-fitting results of C-S stretching region for (a) pure PtBuOA and PtBuOA$_x$LiTFSA (x = 8 − 64) and (b) pure P3CEOA and P3CEOA$_x$LiTFSA (x = 0.8 − 32) at room temperature. IR spectra for LiTFSA dissolved in THF (bottom) and pure LiTFSA powder (top) is also shown for comparison.