Electronic Supplementary Information (ESI)

Ionic Liquid Pillar[5]arene: Its Ionic Conductivity and Solvent-Free Complexation with a Guest

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Experimental section

Materials. All solvents and reagents were used as supplied. *per*-Ethylated pillar[5]arene (**C2**) was synthesized according to the previous paper.[1]

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Thermogravimetric analysis was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere. Ionic conductivity was measured with a complex-impedance gain-phase analyzer (Solartron model 1260; Schlumberger) in the frequency range from 1 Hz to 1 MHz. The samples were thoroughly dried under vacuum at 60 ^{o}C for 24 h prior to the measurements. The samples were sandwiched in a cell constructed with a pair of stainless steel plates. UV-Vis absorption spectra were recorded with a JASCO V-670. For UV-Vis measurements, one centimeter quartz cuvets were used.

Determination of association constant. The association constant (K) of tetracyanoethylene (TCNE)-**C2** complex was determined by probing the charge-transfer (CT) band of the complex by UV-Vis spectroscopy and employing titration method. Addition of **C2** to a chloroform solution with the same concentration of TCNE resulted in an increase of the intensity of the CT band of the complex. By the non-linear curve-fitting methods, K for the complex in $CHCl_3$ was estimated to be 63.5 ± 4.7 M^{-1} for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:

$$A = (A_{\infty}/[G]_0)(0.5[H]_0+1/K) - (0.5[H]_0^2 + (2[H]_0(1/K - [G]_0)) + (1/K + [G]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where A is the absorption intensity of the CT band at $[H]_0$, A_{∞} is the absorption intensity of the CT band when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the initial concentration of the host.

4. To a solution of bis(1-bromopropoxy)benzene[2] (**3**, 1.00 g, 2.84 mmol) and paraformaldehyde (0.269 g, 8.97 mmol) in 1,2-dichloroethane (20 mL), BF_3▪OEt_2 (0.360 mL, 2.86 mmol) was added. The mixture was stirred at 30 ^{o}C for 30 min under nitrogen atmosphere. The resulting solution was poured into methanol and the precipitate was collected by filtration. Column chromatography (silica gel; hexane : dichloromethane = 3 : 2) afforded an white solid (**4**, 454 mg, 0.249 mmol, Yield: 44%).

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.74 (s, 10H, phenyl), 3.99 (t, J = 6 Hz, 20H, methylene), 3.76 (s, 10H, methylene bridge), 3.52 (t, J = 6 Hz, 20H, methylene), 2.23 (m, 20H, methylene). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 149.8, 128.5, 115.3 (C of phenyl), 66.3, 32.7, 30.4 (C of methylene), 29.8 (C of methylene bridge). Anal. Calcd for $C65H80Br10O10 \cdot 0.20C_6H_{14}$ C, 43.27; H, 4.54; N, 0.00. Found: C, 43.30; H, 4.56; N, 0.00. FABMS: *m*/*z* Calcd for C65H85O10Br10 $[M]^+$:1820, found 1820.

1-Br. To a solution of 1-methylimidazole (5 mL), **4** (50.0 mg, 0.0275 mmol) was added. The mixture was heated at 80 °C for 24 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times. (**1-Br**, 60 mg, 0.0227 mmol, Yield: 83%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 9.21 (br, 10H, imidazolium), 8.01 (br, 10H, imidazolium), 7.57 (br, 10H, imidazolium), 6.75 (s, 10H, phenyl), 4.51 (br, 20H, methylene), 3.85-4.20 (br, 20H, methylene), 3.76 (s, 30H, methyl), 3.60 (s, 10H, methylene bridge), 2.36 (m, 20H, methylene). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 149.4 (C of phenyl), 137.0 (C of imidazolium), 128.3 (C of phenyl), 124.0, 122.8 (C of imidazolium), 114.6 (C of phenyl), 65.6, 46.8 (C of methylene), 36.3 (C of methyl), 30.6 (C of methylene), 29.2 (C of methylene bridge). Anal. Calcd for $C105H140Br10N20O10 \cdot 11.7H_2O$ C, 44.22; H, 5.77; N, 9.82. Found: C, 44.16; H, 5.70; N, 9.75. ESIMS (CH_3OH): *m*/*z* Calcd for C105H140Br8N20O10 $[M-2Br]^{2+}$: 1240, found 1240.

1-PF$_6$. To a solution of **1-Br** (60 mg, 0.0227 mmol) in water (10 mL), $NaPF_6$ (70 .0 mg, 0.417 mmol) was added. The reaction mixture was stirred at 25 °C for 10 min. The precipitate was collected by filtration. (**1-PF$_6$**, 54.0 mg, 0.0164 mmol, Yield: 72%). ^{1}H NMR (CD_3CN, 500 MHz, ppm): δ 8.11 (s, 10H, imidazolium), 7.33 (br, 10H, imidazolium), 7.10 (br, 10H, imidazolium), 6.77 (s, 10H, phenyl), 4.35 (t, J = 7 Hz, 20H, methylene), 3.93 (br, 20H, methylene), 3.70 (s, 10H, methylene bridge), 3.66 (s, 30H, methyl), 2.33 (m, 20H, methylene). ^{13}C NMR (CD_3CN, 125 MHz, ppm): δ 150.4 (C of phenyl), 137.0 (C of imidazolium), 129.7 (C of phenyl), 124.8, 123.2 (C of imidazolium), 115.3 (C of phenyl), 65.9, 47.9 (C of methylene), 36.8 (C of methyl), 30.9 (C of methylene), 29.7 (C of methylene bridge). Anal. Calcd for $C105H140F60N20O10P10 \cdot H_2O$ C, 38.10; H, 4.32; N, 8.46. Found: C, 37.84; H, 4.36; N, 8.23. HRESIMS (CH_3CN): *m*/*z* Calcd for C105H140F48N20O10P6 $[M-PF_6]^+$: 3000.81957, found 3000.81965.

1-TFSA. To a solution of **1-Br** (50 mg, 0.0189 mmol) in DMF (10 mL) and methanol

(0.5 mL), LiTFSA (0.163 g, 0.570 mmol) was added. The reaction mixture was stirred at 25 °C for 168 h. The resulting solution was poured into water and the precipitate was collected by certification. The reprecipitation process was repeated three times. (**1-TFSA**, 70.0 mg, 0.0151 mmol, Yield: 80%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 9.10 (s, 10H, imidazolium), 7.73 (br, 10H, imidazolium), 7.71 (br, 10H, imidazolium), 6.74 (s, 10H, phenyl), 4.36 (t, J = 8 Hz, 20H, methylene), 3.7-4.1 (br, 20H, methylene), 3.85 (s, 30H, methyl), 3.63 (s, 10H, methylene bridge), 2.27 (m, 20H, methylene). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 149.3 (C of phenyl), 137.1 (C of imidazolium), 128.7 (C of phenyl), 124.4, 122.7 (C of imidazolium), 121.3 (C of TFSA), 118.7 (C of phenyl), 65.4, 46.9 (C of methylene), 36.4 (C of methyl), 30.2 (C of methylene), 29.4 (C of methylene bridge). Anal. Calcd for C125H140F60N30O50S20 C, 32.33; H, 3.04; N, 9.05. Found: C, 32.79; H, 3.24; N, 9.14. HRFABMS (CH_3OH): *m*/*z* Calcd for C121H140F48N28O42S16H70N7O2 [M-TFSA]$^{+}$: 4080.44447, found 4080.44505.

2-TFSA. To a solution of 1-methylimidazole (6.72 mL), bis(1-bromopropoxy)benzene (**3**, 1.00 g, 2.84 mmol) was added. The mixture was heated at 80 °C for 24 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times (**2-Br**, 1.26 g, 2.44 mmol, Yield: 86%). To a solution of **2-Br** (200 mg, 0.387 mmol) in DMF (10 mL) and methanol (0.5 mL), LiTFSA (1.11 g, 3.87 mmol) was added. The reaction mixture was stirred at 25 °C for 168 h. The resulting solution was poured into water and the precipitate was collected by filtration. The reprecipitation process was repeated twice. (**2-TFSA**, 242 mg, 0.264 mmol, Yield: 68%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 9.12 (s, 2H, imidazolium), 7.78 (br, 2H, imidazolium), 7.70 (br, 2H, imidazolium), 6.83 (s, 4H, phenyl), 4.33 (t, J = 7 Hz, 4H, methylene), 3.94 (t, J = 6 Hz, 4H, methylene), 3.84 (s, 6H, methyl), 2.24 (m, 4H, methylene). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 153.0 (C of phenyl), 137.3 (C of imidazolium), 124.1, 123.0 (C of imidazolium), 121.3 (C of TFSA), 118.7 (C of phenyl), 65.4, 47.0 (C of methylene), 36.3 (C of methyl), 29.7 (C of methylene). Anal. Calcd for C24H28F12N6O10S4 C, 31.44; H, 3.08; N, 9.17. Found: C, 31.48; H, 3.33; N, 9.10. HRESIMS: *m*/*z* Calcd for C22H28F6N5O6S2 [M-TFSA]$^{+}$: 636.13852, found 636.13848.

^{1}H and ^{13}C NMR spectra of 4

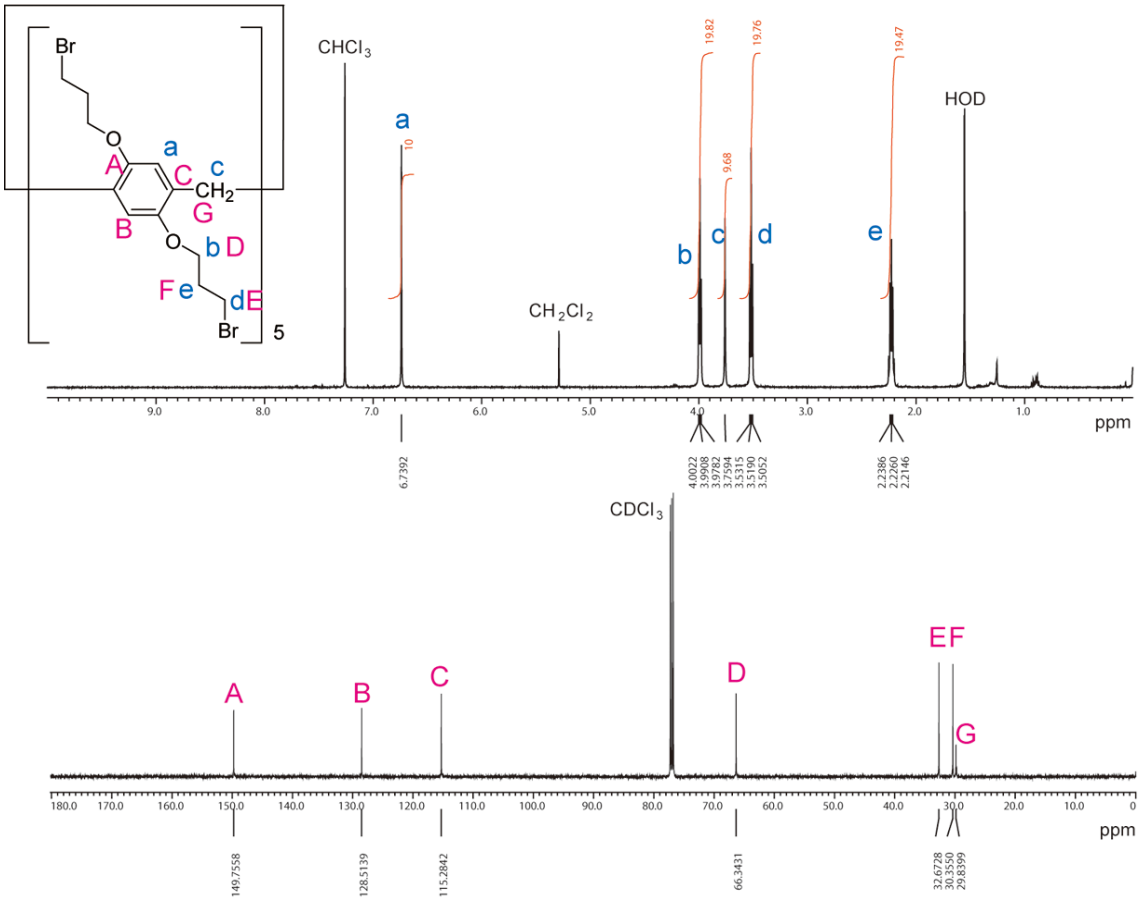

Fig. S1 ^{1}H and ^{13}C NMR spectra of **4** in $CDCl_3$ at 25 ^{o}C.

^{1}H and ^{13}C NMR spectra of 1-Br

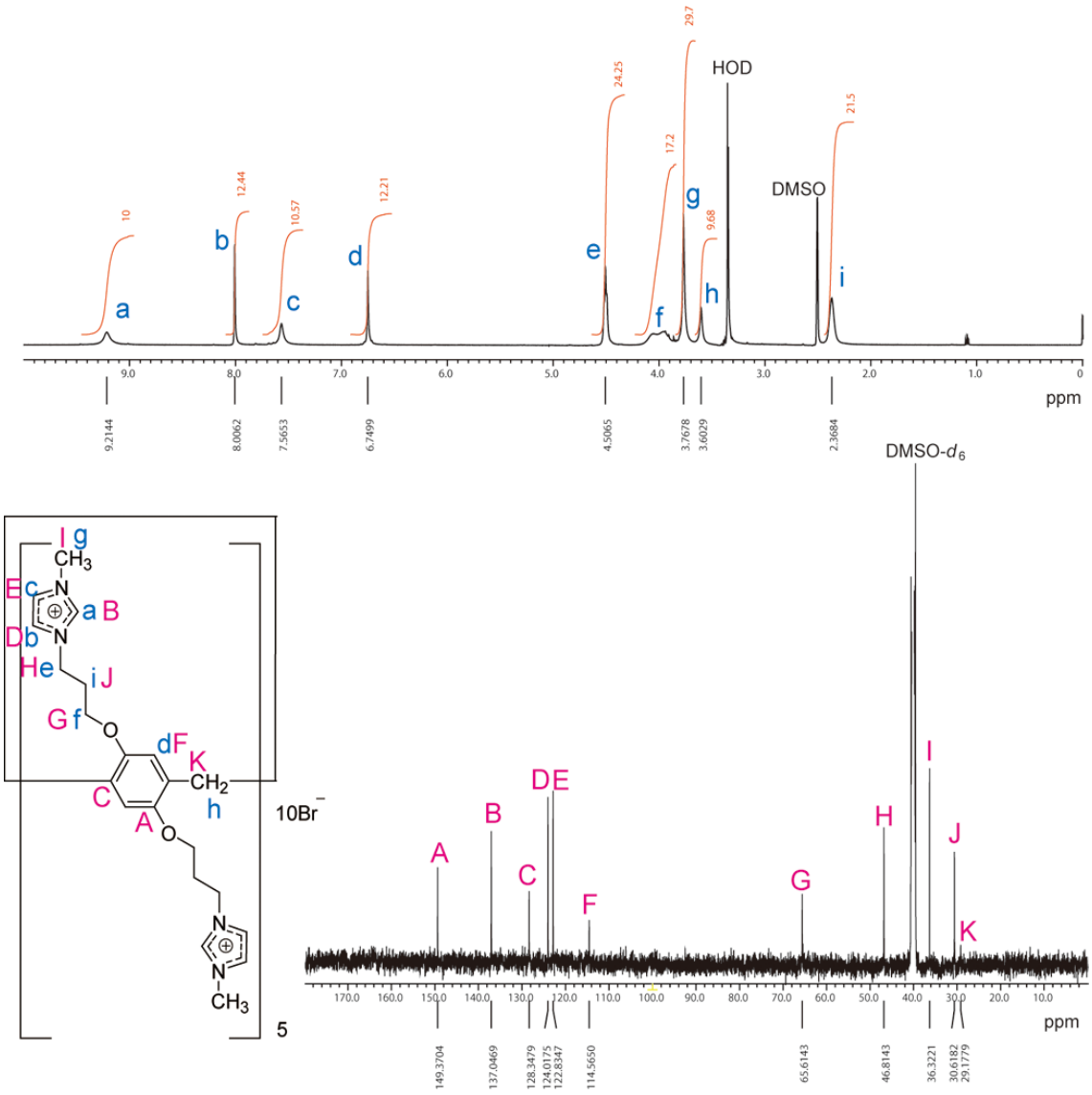

Fig. S2 ^{1}H and ^{13}C NMR spectra of **1-Br** in DMSO-d_6 at 25 ^{o}C.

^{1}H and ^{13}C NMR spectra of 1-PF_6

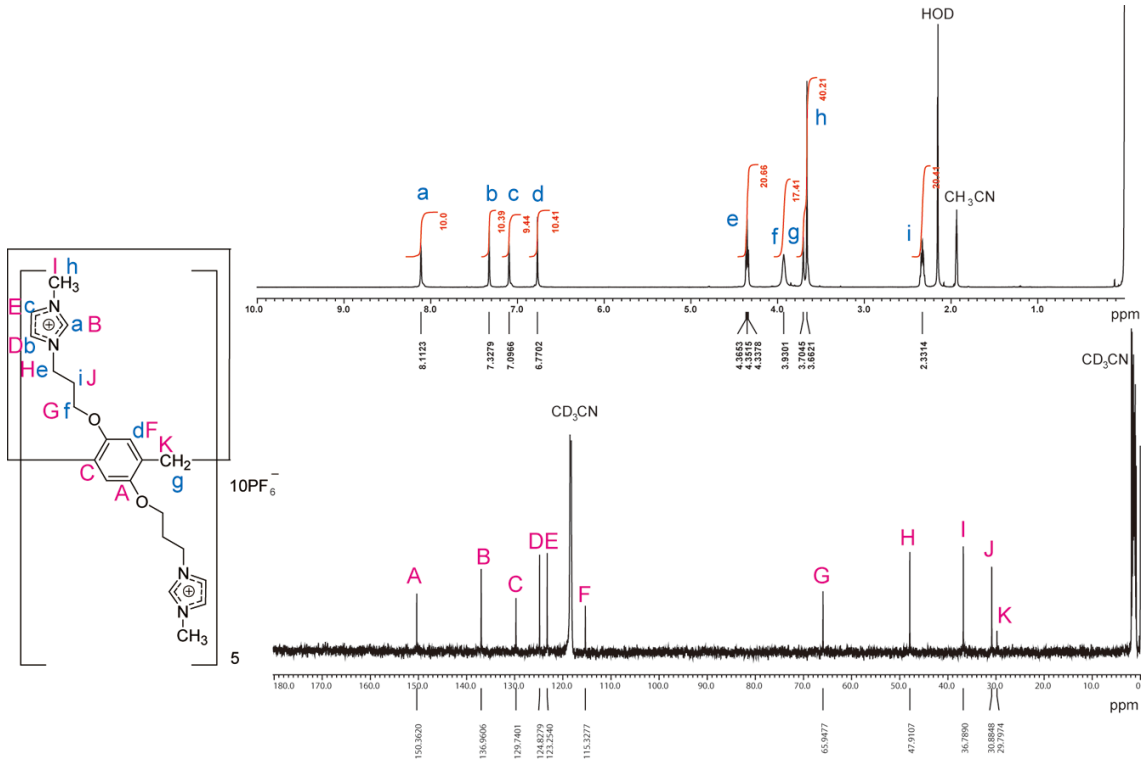

Fig. S3 ^{1}H and ^{13}C NMR spectra of **1-PF_6** in CD_3CN at 25 ^{o}C.

HRESIMS spectra of 1-PF_6

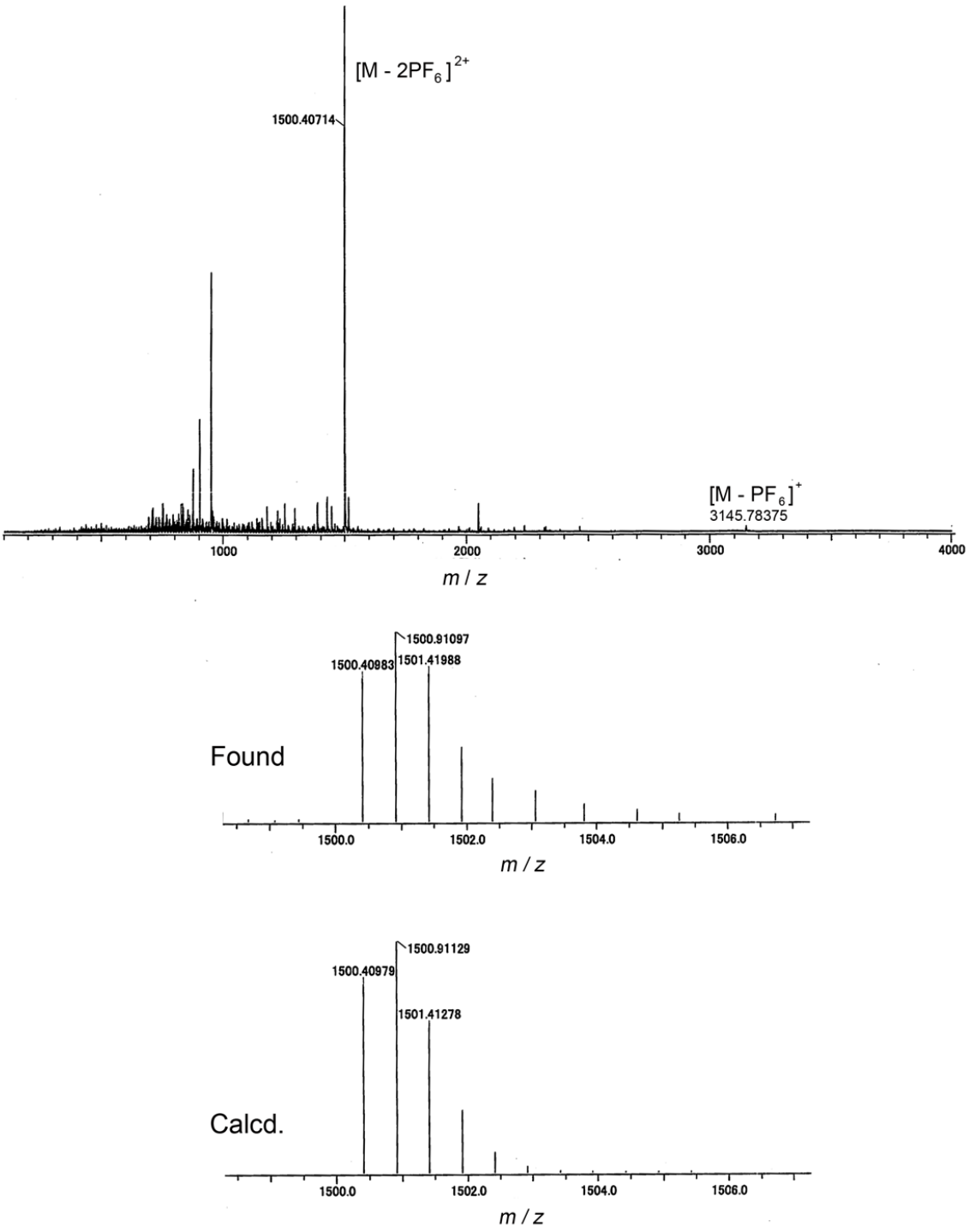

Fig. S4 HRESIMS spectra (CH_3CN) of **1-PF_6**.

^{1}H and ^{13}C NMR spectra of 1-TFSA

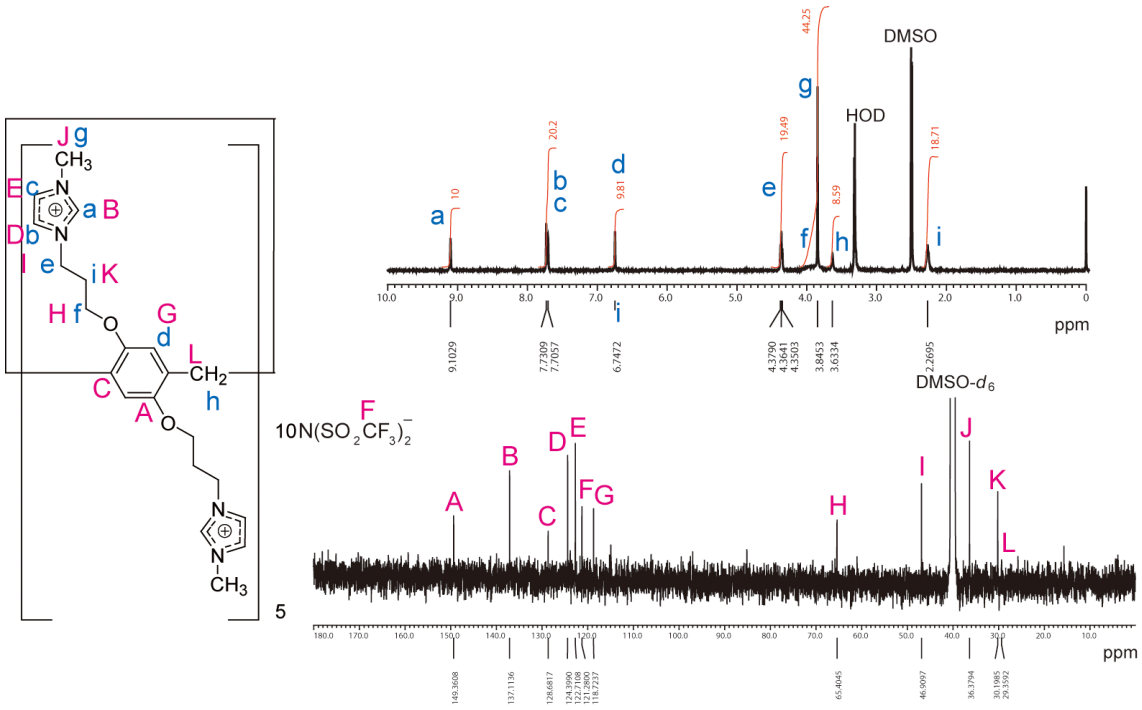

Fig. S5 ^{1}H and ^{13}C NMR spectra of **1-TFSA** in DMSO-d_6 at 25 ^{o}C.

HRESIMS spectra of 1-TFSA

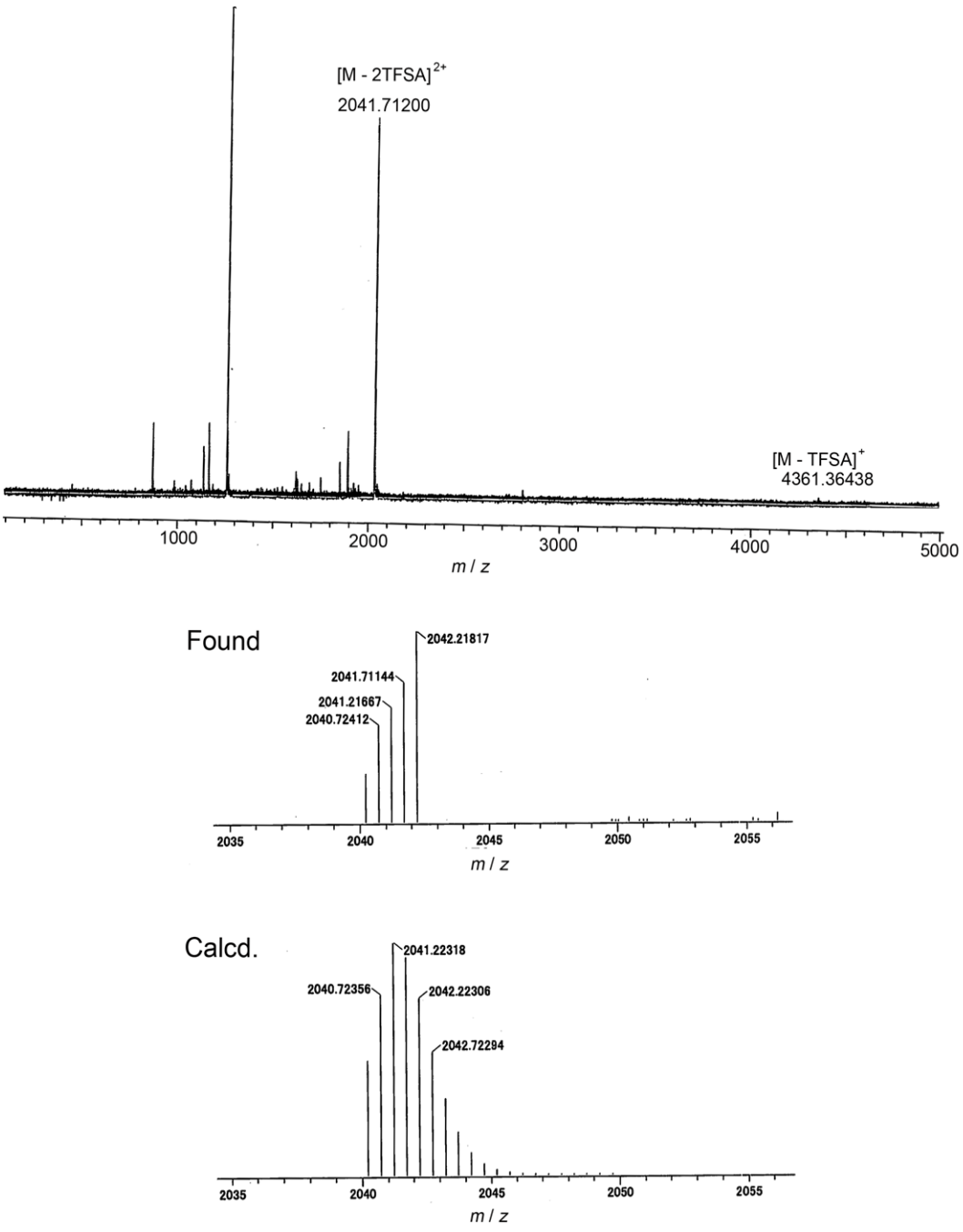

Fig. S6 HRESIMS spectra (CH_3OH) of **1-TFSA$_6$**.

^{1}H and ^{13}C NMR spectra of 2-TFSA

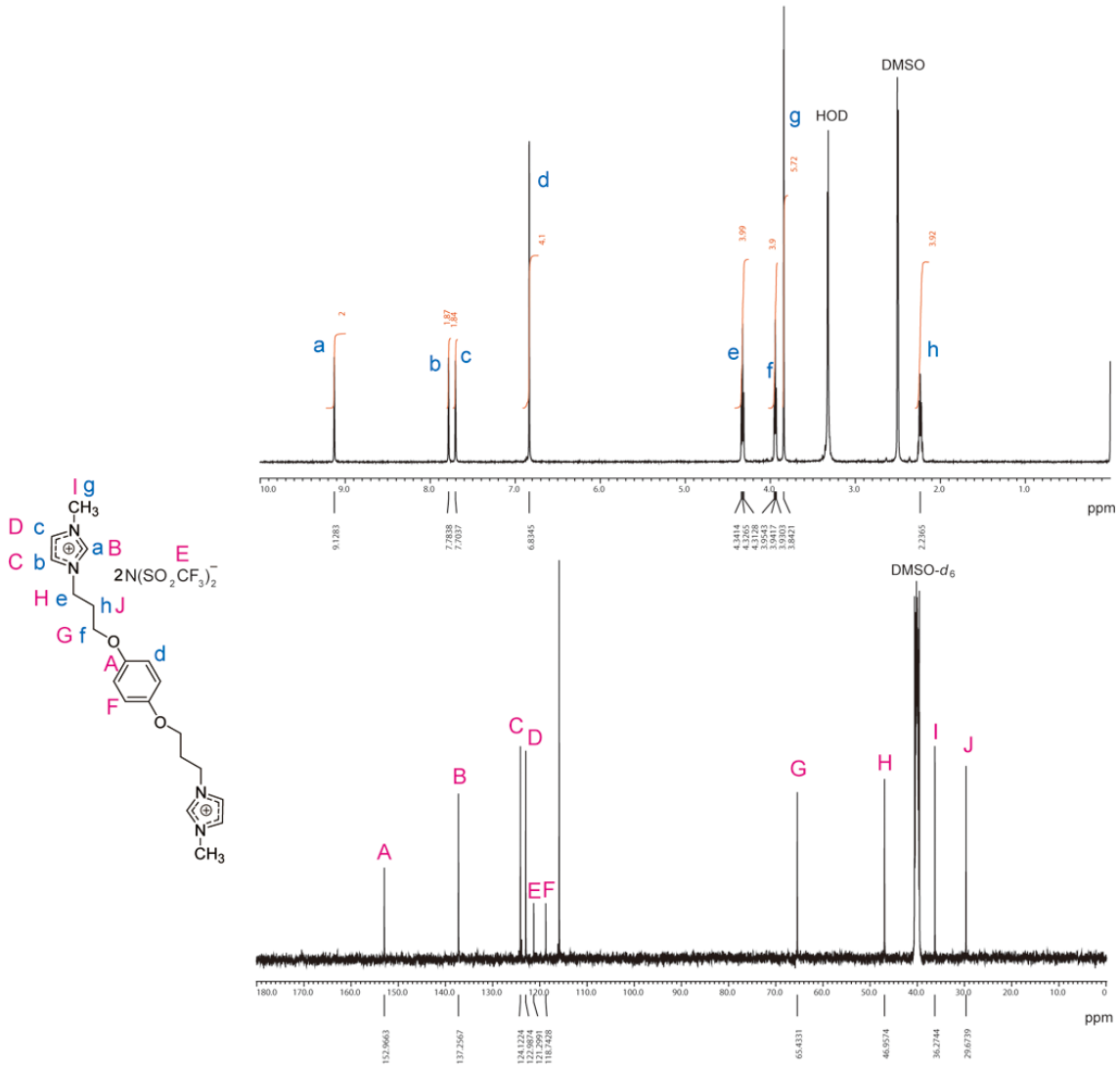

Fig. S7 ^{1}H and ^{13}C NMR spectra of **2-TFSA** in DMSO-d_6 at 25 ^{o}C.

DSC traces of 1-PF_6

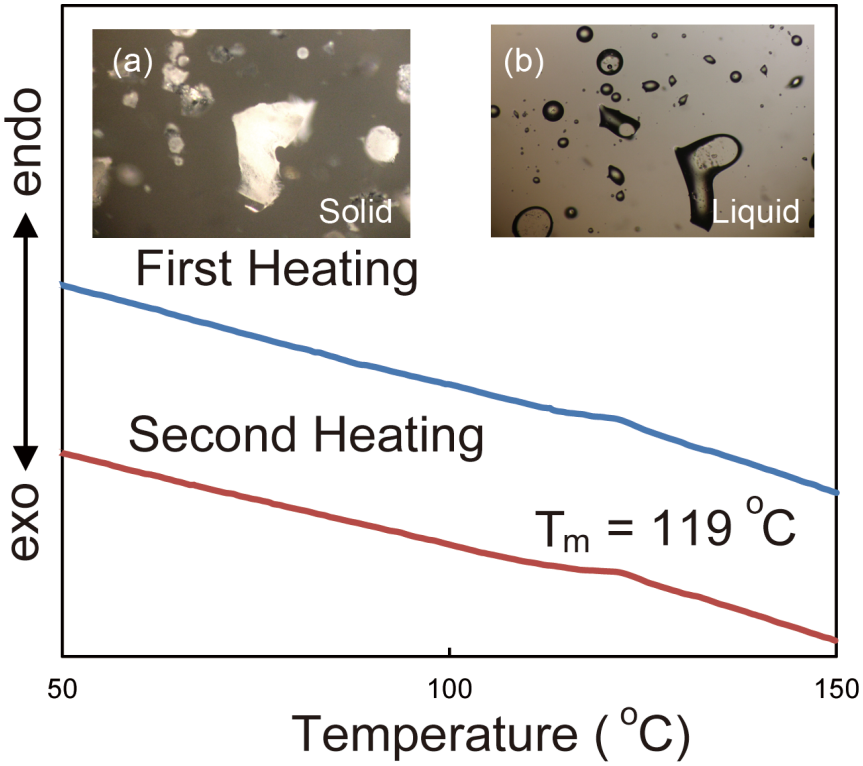

Fig. S8 DSC traces of **1-PF_6** at the multicycle scanning (insert: photographs of optical microscope of **1-PF_6** below (a) and above (b) melting point).

DSC traces of 1-TFSA

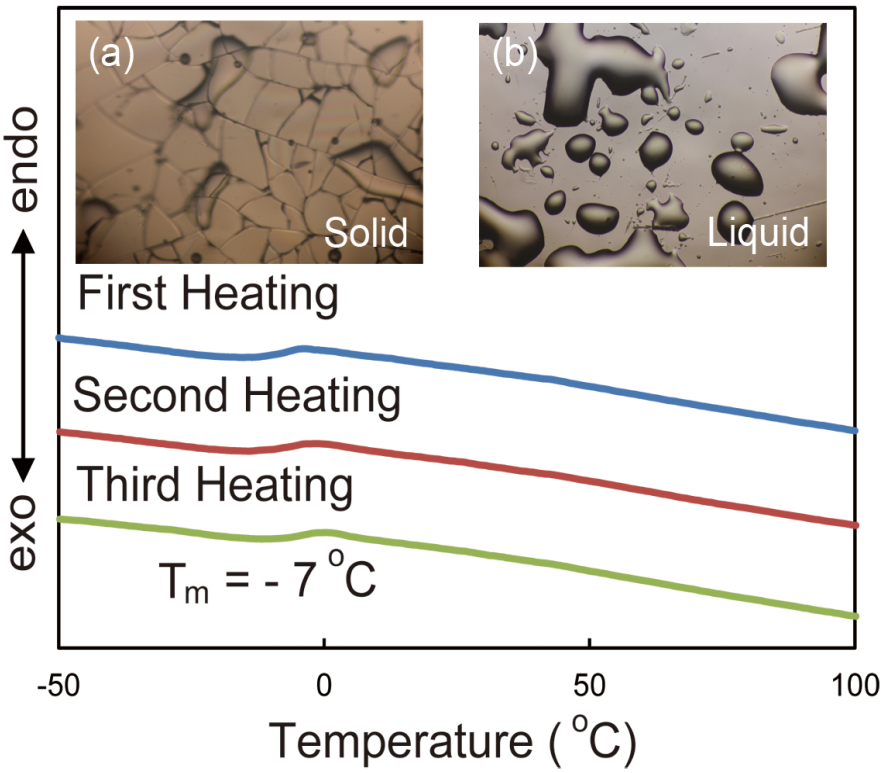

Fig. S9 DSC traces of **1-TFSA** at the multicycle scanning (insert: photographs of optical microscope of **1-PF$_6$** below (a) and above (b) melting point).

DSC traces of 2-TFSA

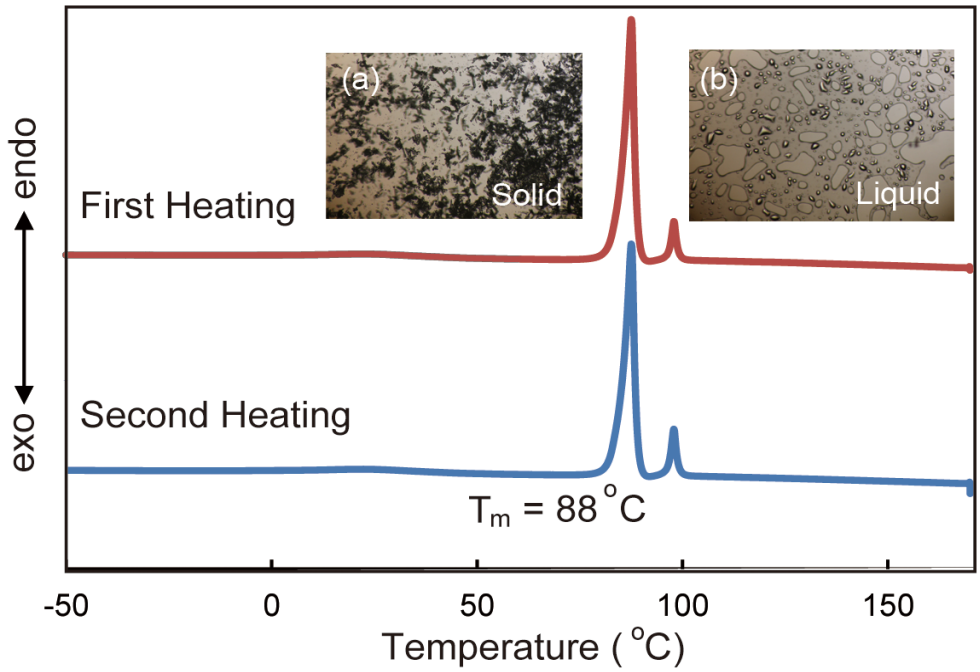

Fig. S10 DSC traces of **1-TFSA** at the multicycle scanning (insert: photographs of optical microscope of **2-TFSA** below (a) and above (b) melting point).

Thermogravimetric analysis of 4 and 1-TFSA

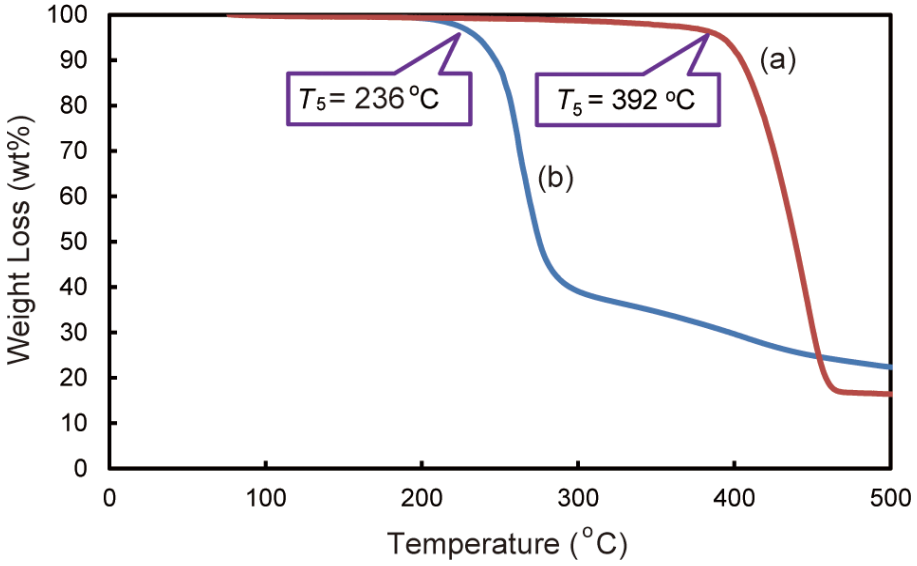

Fig. S11 Thermogravimetric analysis of (a) **1-TFSA** and (b) **4**.

Ionic conductivity of 1-TFSA

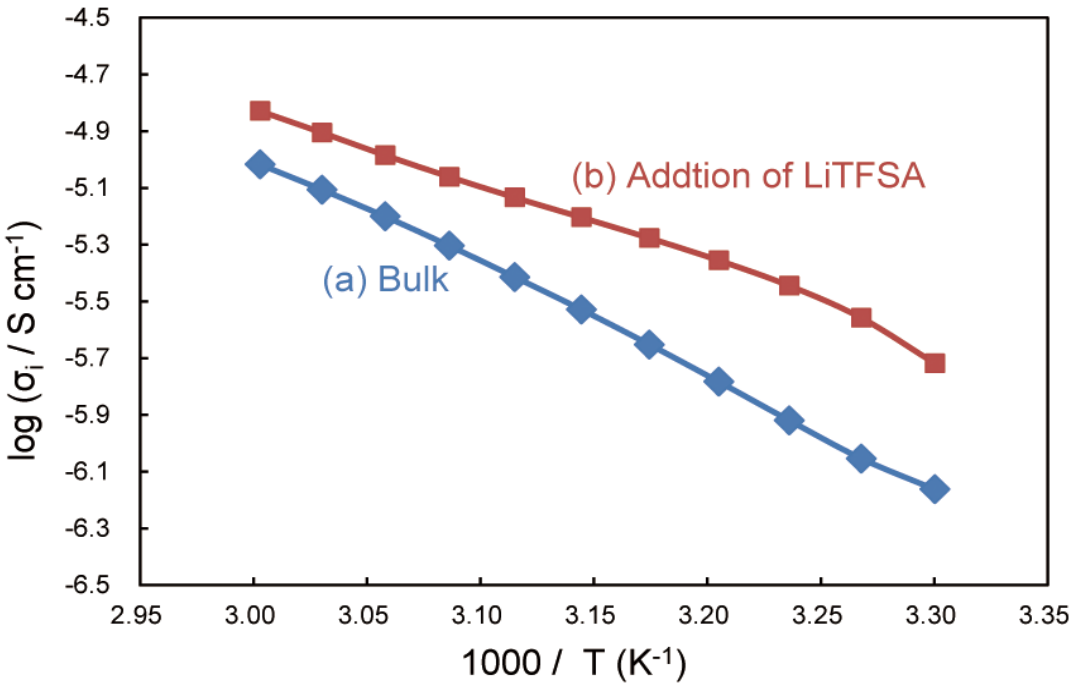

Fig. S12 Temperature dependences of ion conductivity of **1-TFSA** (a) in the bulk and (b) upon addition of an equimolar amount of LiTFSA toward the imidazolium units.

UV-Vis spectra of TCNE and TCNQ with C2

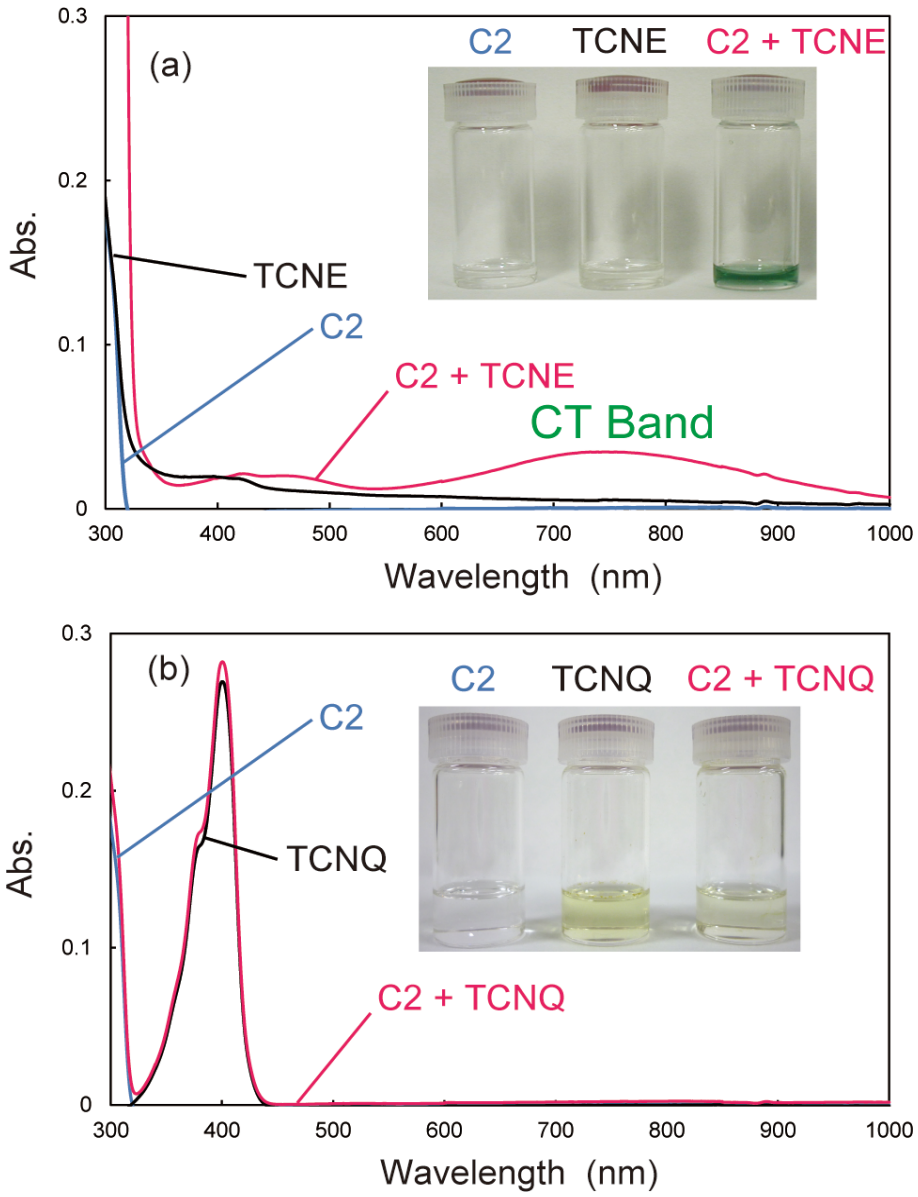

Fig. S13 UV-Vis absorption spectra of (a) **C2** (blue line), TCNE (black line) and an 1:1 mixture of **C2** and TCNE (pink line) and (b) **C2** (blue line), TCNQ (black line) and an 1:1 mixture of **C2** and TCNQ (pink line) in 0.01 mM (insert: photographs of these samples). Observation of the charge-transfer (CT) band indicates complexation between **C2** and TCNE.

Job Plot for a mixture of TCNE and C2

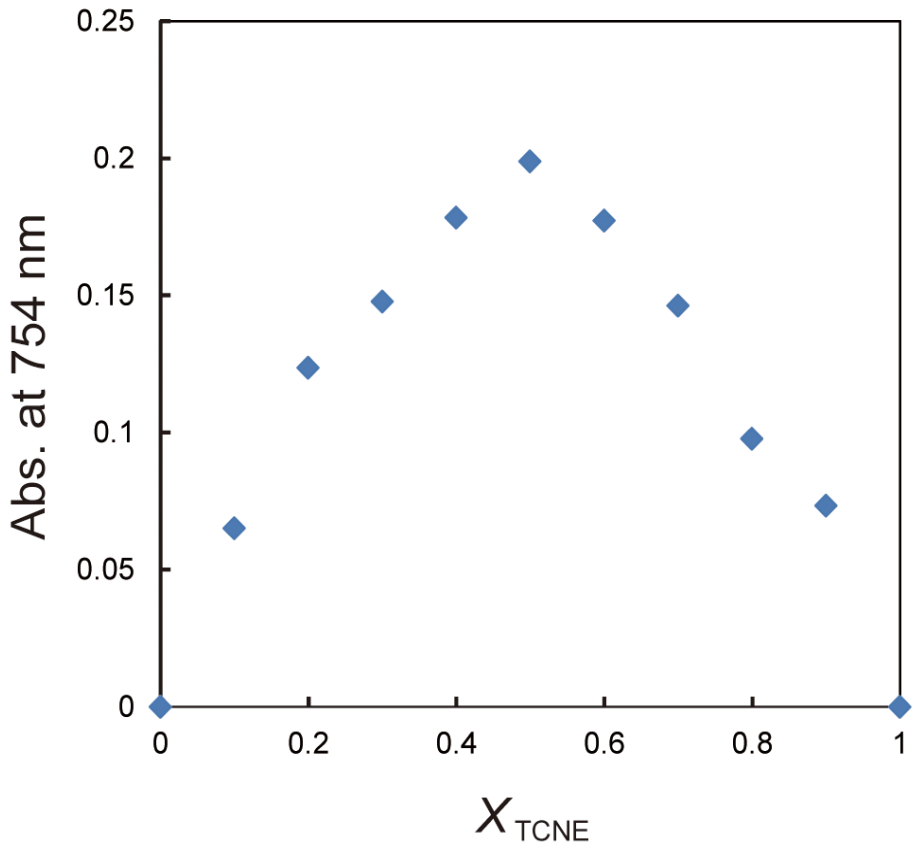

Fig. S14 Job plot between **C2** (host) and TCNE (guest). The job plot was conducted by varying the mole fractions of the guest and host. Absorption bands at 754 nm were utilized. Concentration: [**C2**] + [TCNE] = 2 mM. The plot indicates a 1:1 binding between the host and guest.

UV-Vis titration for TCNE-C2 complex

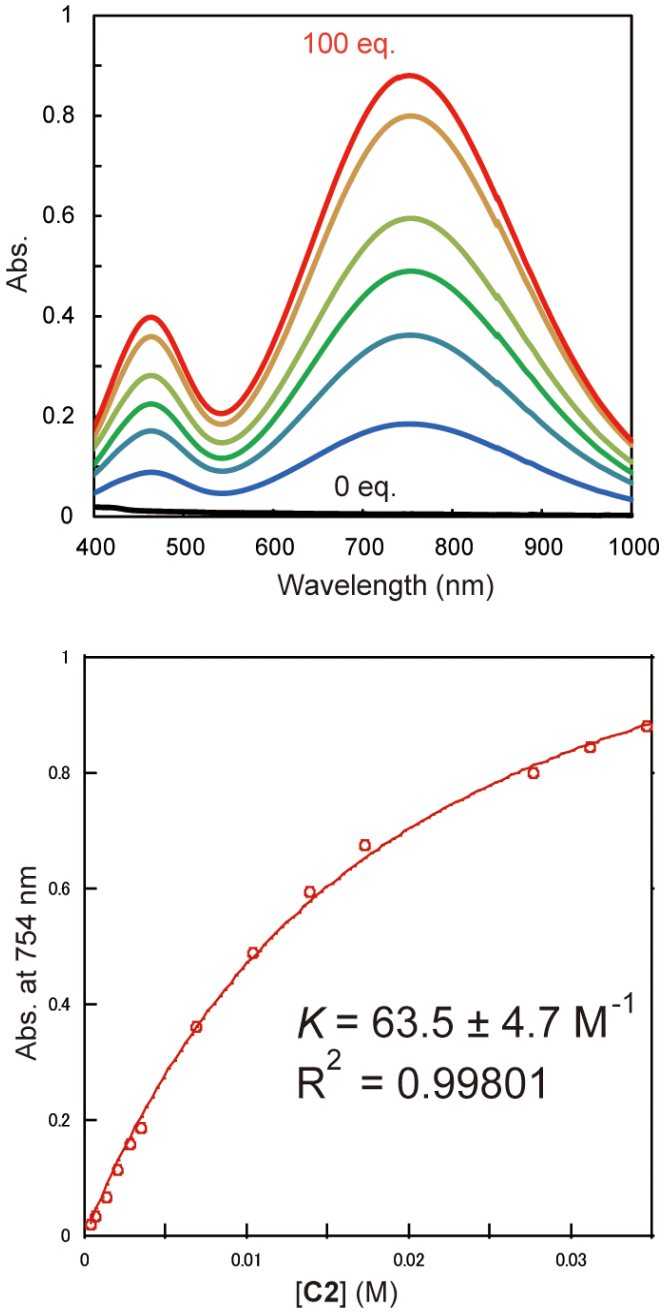

Fig. S15 The absorption spectral changes of TCNE upon addition of **C2** (upper) and the absorbance changes upon addition of **C2** (bottom); [TCNE] = 0.35 mM. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

References

(1) T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.,* 2010, **75**, 3268.
(2) R. Adams and L. N. Whitehill, *J. Am. Chem. Soc.* 1941, **63**, 2073.