Anion Size-Dependent Carbon Dioxide Adsorption Capacity in High-Purity Diallyldimethylammonium-Based Poly(ionic liquid)s

Kohei Okubo,[a] Showa Kitajima,[a, b] Hitoshi Kasai,[a] Kiyotaka Maruoka,[c] Yuta Takahashi,[c] Yoko Teruuchi,[c] Minoru Takeuchi,[c] Kazuhiko Igarashi,[c] and Kouki Oka*[a, d, e]

[a] Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
E-mail: oka@tohoku.ac.jp (Kouki Oka)

[b] Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, 6-6 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

[c] NITTO BOSEKI CO., LTD., 2-4-1 Kojimachi, Chiyoda-ku, Tokyo 102-8489, Japan.

[d] Carbon Recycling Energy Research Center,
Ibaraki University
4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

[e] Deuterium Science Research Unit, Center for the Promotion of Interdisciplinary Education and Research,
Kyoto University
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

1. Measurements.

Infrared (**IR**) spectra were recorded on a Shimadzu IRSpirit instrument equipped with an ATR accessory. Energy-dispersive X-ray (**EDX**) spectra (accelerating voltage: 15 kV) were obtained using a JEOL JSM-7800F instrument. Gas adsorption measurements were performed using a MicrotracBEL BELSORP-max X instrument. The adsorption isotherms were collected at 298 K. Before all measurements, the samples were dried under reduced pressure at 353 K for 3 h. The density functional theory (**DFT**) calculation was carried out using Gaussian 16 software. The B3LYP/6-31+G (d,p) level of theory was chosen to compute the geometry of all the species. Differential scanning calorimetry (**DSC**) curves were obtained using a Shimadzu DSC-60A Plus. The measurements were performed in the temperature range of 0–200 ℃ with heating rate of 10 ℃ min^{-1} and nitrogen flow rate of 50 ml min^{-1}. Since the polymer samples were highly hygroscopic in nature, the glass transition temperatures (T_g) were determined using the two scans. T_g values were determined as the point corresponding to the midpoint inflection of the extrapolated onset and end of the transition curve.

2. Materials.

Poly(diallyldimethylammonium chloride) (**P[DADMA][Cl]**) (M_w = 30000) was provided by NITTO BOSEKI CO., LTD. Potassium acetate (KOAc), sodium thiocyanate

(NaSCN), and silver trifluoromethanesulfonate (AgTFMS) were obtained from Tokyo Chemical Industry Co., Ltd. All reagents were used as received without further purification.

3. Synthesis of P[DADMA][SCN]

P[DADMA][Cl] (500 mg, 3.09 mmol) was added to water (30 mL) and NaSCN (502 mg, 6.18 mmol) was added at room temperature and stirred for 24 h. Subsequently, the mixture was dissolved in 0.25 M NaSCN aqueous solution, dialyzed for 24 h, and then concentrated under reduced pressure using an evaporator. The residue was dissolved in 10 mL of water, dialyzed for 24 h in 1 L of water, and placed in a freeze dryer. After one day of drying, a yellow solid (312 mg, 1.67 mmol, 54%) was obtained.

4. Synthesis of P[DADMA][TFMS]

P[DADMA][Cl] (216 mg, 1.33 mmol) was added to water (30 mL), and AgTFMS (340 mg, 1.33 mmol) and water (1 mL) were added drop-wise at room temperature and stirred overnight. The reaction mixture was centrifuged at 3000 rpm for 1.5 h. The supernatant was dialyzed and placed in a freeze dryer. After drying for one day, a pale-orange solid (219 mg, 0.80 mmol, 60%) was obtained.

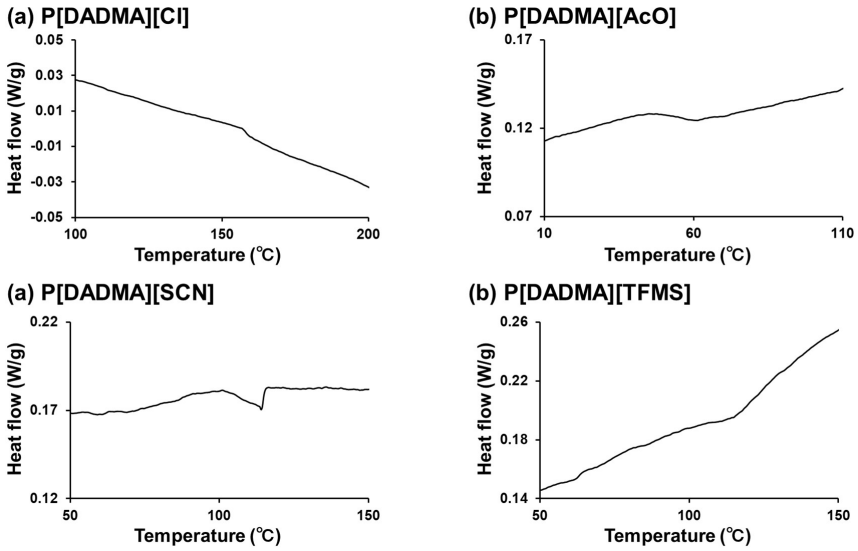

Figure S1. DSC curves of (a) **P[DADMA][Cl]**, (b) **P[DADMA][AcO]**, (c) **P[DADMA][SCN]**, and (d) **P[DADMA][TFMS]**.

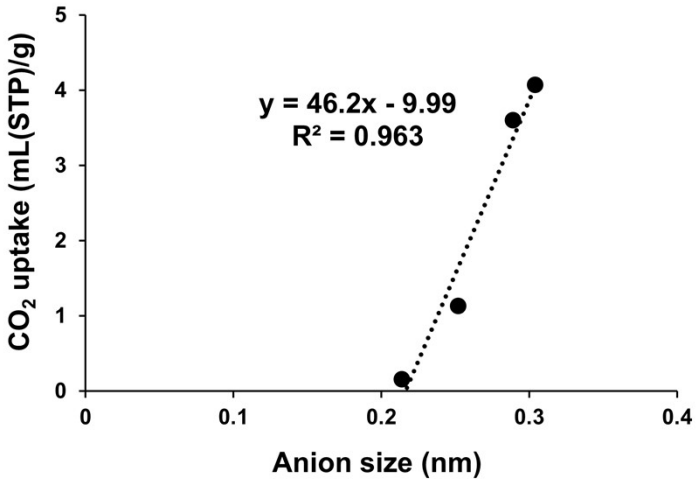

Figure S2. Correlation between anion size and CO_2 adsorption capacity.

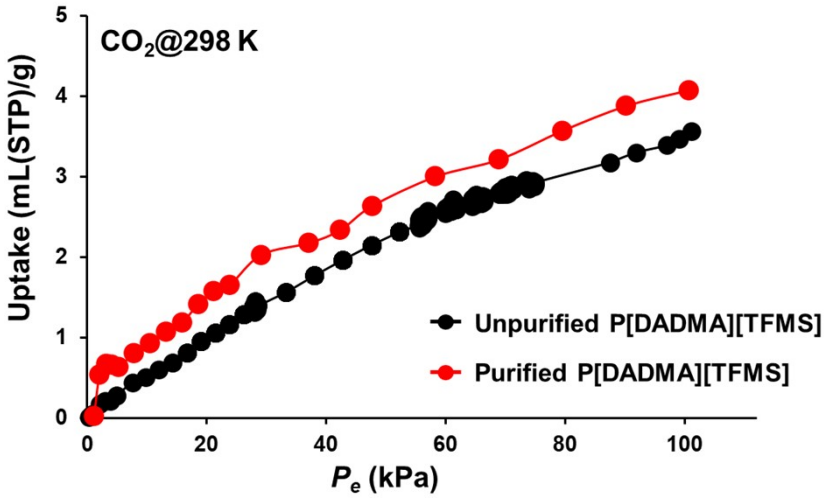

Figure S3. CO_2 adsorption isotherms of unpurified **P[DADMA][TFMS]** (black) and purified **P[DADMA][TFMS]** (red) at 298 K.

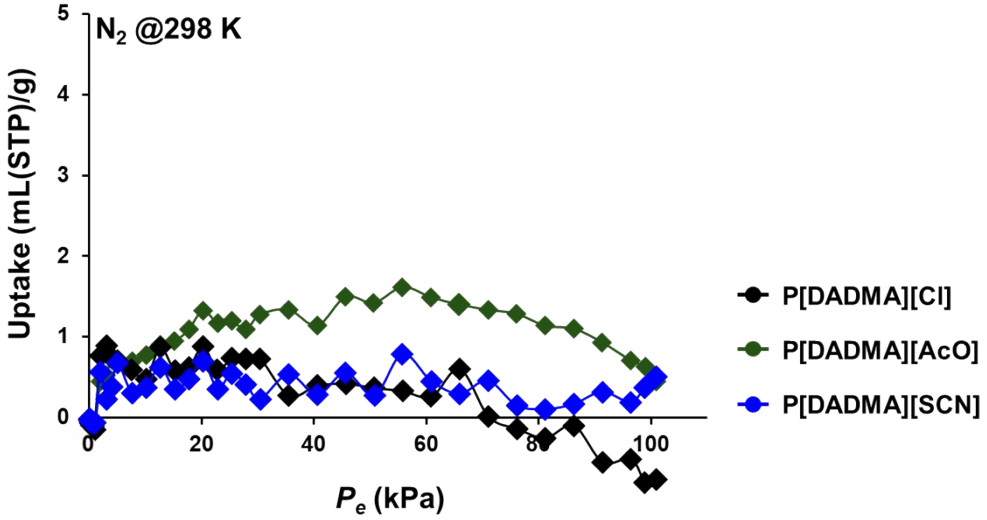

Figure S4. N_2 adsorption isotherms of **P[DADMA][Cl]** (black), **P[DADMA][AcO]** (green), and **P[DADMA][SCN]** (blue) at 298 K.

Table S1. Assignment of **IR** spectra of **P[DADMA][Cl]**.

Assignments	Wave number / cm^{-1}
C-H bending	946
C-N stretching	1101
C-H bending	1457
C-H stretching	2930

Table S2. Assignments of **IR** spectrum of **P[DADMA][AcO]**.

Assignments	Wave number / cm^{-1}
C-H bending	986
C-N stretching	1063
COO^- symmetric stretching	1374
C-H bending	1461
COO^- asymmetric stretching	1625
C-H stretching	2934

Table S3. Assignments of **IR** spectrum of **P[DADMA][SCN]**.

Assignments	Wave number / cm^{-1}
C-H bending	945
C-N stretching	1087
C-H bending	1466
C-N stretching	2045
C-H stretching	2929

Table S4. Assignments of **IR** spectrum of **P[DADMA][TFMS]**.

Assignments	Wave number / cm^{-1}
CF_3 bending (**[TFMS]**)	573
SO_3 bending	636
C-S stretching	757
C-H bending	945
O=S=O stretching	1027
C-N stretching	1150
C-F stretching	1251

C-H bending	1474
C-H stretching	2933

Table S5. Glass transition temperature (T_g) of each **PIL**.

Sample	T_g / ℃
P[DADMA][Cl]	158.2
P[DADMA][AcO]	53.26
P[DADMA][SCN]	108.6
P[DADMA][TFMS]	107.5

Cartesian coordinates of optimized geometries

Cl^-

Atom	X	Y	Z
Cl	0	0	0

AcO^-

Atom	X	Y	Z
C	-1.3540513	-0.0488433	0.0000425
H	-1.7272307	-1.0788186	0.0032619
H	-1.7386201	0.4762242	-0.8841882
H	-1.7392097	0.4822302	0.8804176
C	0.2091255	0.0011716	0.0000754
O	0.8042422	-1.1112714	-0.0000148
O	0.7050848	1.1620707	-0.00001

SCN^-

Atom	X	Y	Z
C	0	0	-0.63709

N	0	0	-1.81986
S	0	0	1.035099

TFMS$^-$

Atom	X	Y	Z
S	-0.9398357	0.0000002	-0.0000023
C	0.9527405	-0.0000075	0.0000004
O	-1.2552989	-0.1226977	1.44276
O	-1.2552806	1.3108218	-0.6151253
O	-1.2553123	-1.1881198	-0.8276382
F	1.4610477	0.1065871	-1.2528168
F	1.4610482	-1.1382742	0.5341017
F	1.4610221	1.031688	0.7187221