Supplementary Materials: Role of Cation Structure in CO2 Separation by Ionic Liquid/Sulfonated Polyimide Composite Membrane

Eri Hayashi [1], Kei Hashimoto [1], Morgan L. Thomas [1,§], Seiji Tsuzuki,[2] and Masayoshi Watanabe [1,*]

[1] Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[2] Research Center for Computational Design of Advanced Functional Materials (CD-FMat), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

[§] Present address: Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan

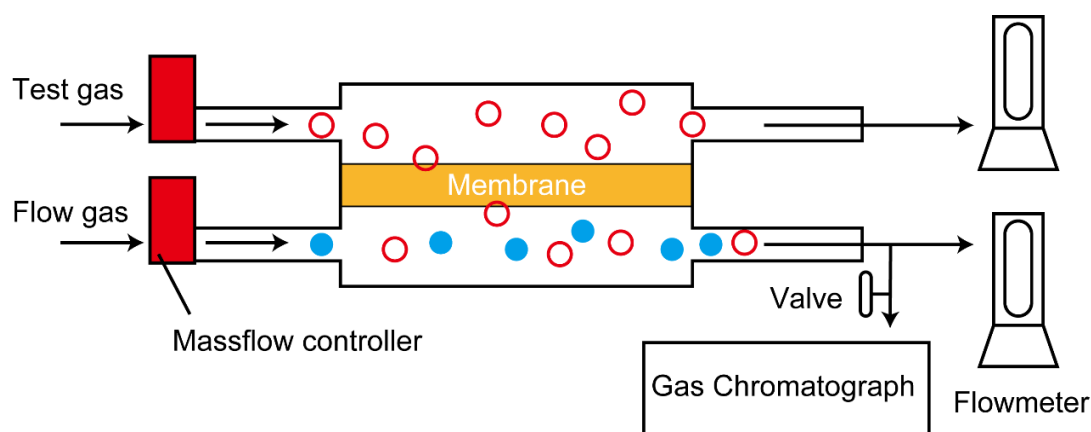[*] Correspondence: mwatanab@ynu.ac.jp; Tel.: +81- 45-339-3955

Figure S1. A sketch of gas permeation test.

Table S1. Decomposition temperatures of ion gels obtained by TG.

	[C3imH][NTf2]	[C2mim][NTf2]
	T_d / °C [a]	T_d / °C [a]
IL	353.6	401.5
IL/SPI composite [b]	325.4	334.3
SPI	268.6	

[a] Decomposition temperature (T_d) is defined as the temperature at 5% weight loss.

[b] IL content of IL/SPI composite membrane is 75 wt%.

Table S2. Melting temperature (T_m) and glass transition temperature (T_g) for [C3imH][NTf2] and [C2mim][NTf2].

	[C3imH][NTf2]	[C2mim][NTf2][a]
T_m / °C	4.8	−12.1, −2.7
T_g / °C	−87.1	−94.0

Table S3 The results of gas permeability measurements performed under single gas conditions at 30 °C.[a]

	[C2mim][NTf2]	[C3imH][NTf2]
P_{CO_2}	430	295
P_{N_2}	13.7	11.4
α	31	26

[a]P_{CO_2} / P_{N_2}. Unit of gas permeability coefficient (P) is Barrer.

Table S4. CO_2 absorption properties of [C3imH][NTf2] at 30 °C.[a]

P (MPa)	x_{CO_2}	c_{CO_2} (mol/l)	ρ^L (g/cm³)	ΔV^L (%)
0	0	0	1.49	0
0.66	0.15	0.65	1.50	1.16
1.36	0.26	1.32	1.50	2.97
1.86	0.33	1.82	1.50	4.68
2.16	0.37	2.13	1.50	5.88
2.67	0.43	2.67	1.49	8.21
3.42	0.50	3.44	1.48	12.35
3.99	0.55	4.04	1.46	15.98
4.53	0.59	4.53	1.44	19.91
5.03	0.62	4.93	1.42	23.90

[a] x_{CO_2}, c_{CO_2}, ρ^L and ΔV^L correspond to the mole fraction of CO_2, molarities of CO_2, densities and volume expansions of the liquid phase, respectively, in the CO_2/[C3mimH][NTf2] system.

Table S5. CO_2 absorption properties of [C2mim][NTf2] at 30 °C.[a]

P (MPa)	x_{CO_2}	c_{CO_2} (mol/l)	ρ^L (g/cm³)	ΔV^L (%)
0	0	0	1.51	0
0.61	0.14	0.64	1.52	1.36
1.17	0.24	1.19	1.52	2.82
1.74	0.32	1.77	1.52	4.69
2.26	0.39	2.33	1.52	6.75
3.06	0.47	3.16	1.50	10.55
3.65	0.52	3.75	1.49	13.82
4.24	0.57	4.35	1.48	17.57
4.72	0.60	4.76	1.46	20.86
5.20	0.62	5.15	1.44	24.50

[a] x_{CO_2}, c_{CO_2}, ρ^L and ΔV^L correspond to the mole fraction of CO_2, molarities of CO_2, densities and volume expansions of the liquid phase, respectively, in the CO_2/[C2mim][NTf2] system.
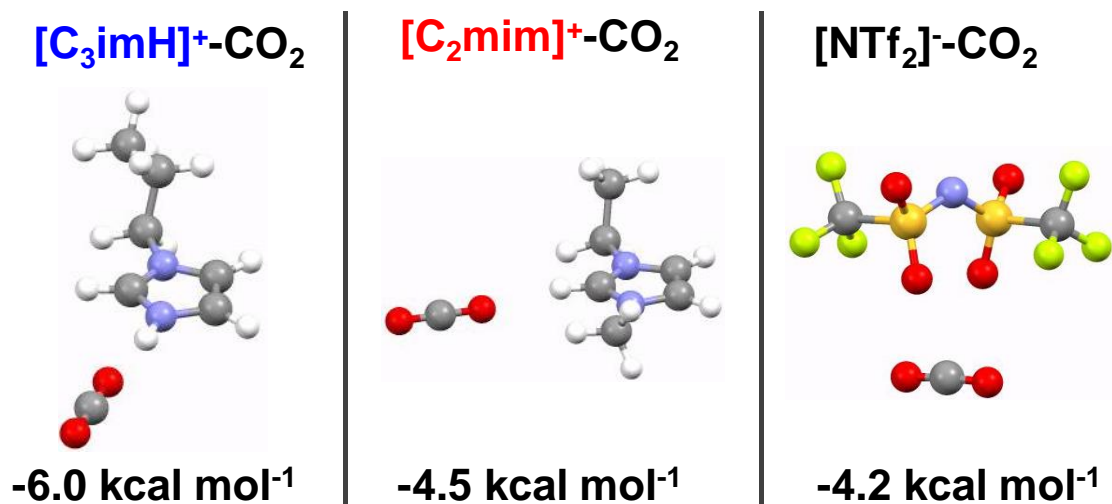
$[C_3imH]^+$-CO_2 **$[C_2mim]^+$-CO_2** **$[NTf_2]^-$-CO_2**

-6.0 kcal mol^{-1} **-4.5 kcal mol^{-1}** **-4.2 kcal mol^{-1}**

Figure S2. The most stable structures of $[C_3imH]^+$–CO_2, $[C_2mim]^+$–CO_2, and $[NTf_2]^-$–CO_2 complexes and their stabilization energies. Geometries were optimized at HF/6-311G** level. Stabilization energies were calculated at MP2/6-311G** level using the optimized geometries. Energy in kcal/mol.

Table S6 The elastic modulus (E), fracture stress (σ_f), fracture strain (λ_f), and fracture energy (W_f) of IL/SPI membranes.

IL[a]	E (MPa)	σ_f (MPa)	λ_f (%)	W_f (kJ/m³)
AIL	3.1	6.3	194	7098
PIL	2.6	5.3	201	6004

[a] AIL:$[C_2mim][NTf_2]$; PIL:$[C_3imH][NTf_2]$ (IL content : 75 wt%).