Fundamental Investigation of the Factors Controlling the CO_2 Permeability of Facilitated Transport Membranes Containing Amine-Functionalized Task-Specific Ionic Liquids

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SUPPLEMENTARY MATERIALS

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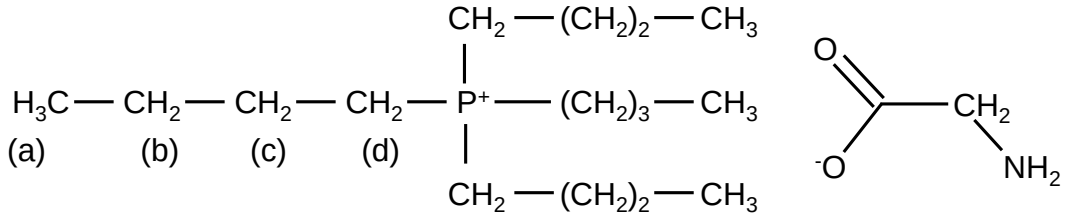
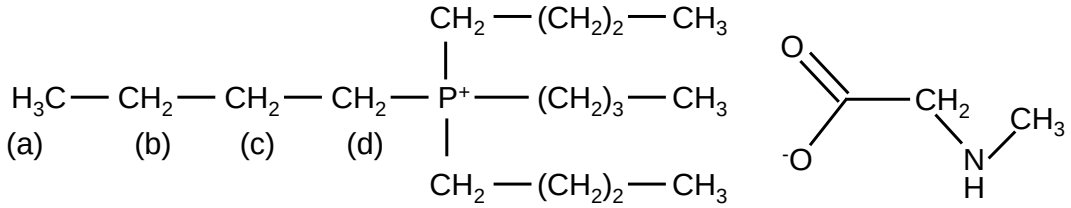
(1) ^{1}H-NMR data of the ILs synthesized in this study

Tetrabutylphosphonium glycinate ([P_{4444}][Gly]), Tetrabutylphosphonium N-methylglycinate ([P_{4444}][mGly]), Tetrabutylphosphonium N,N-dimethylglycinate ([P_{4444}][dmGly]) and Tetrabutylphosphonium 2-cyanopyrrolide ([P_{4444}][2-CNpyr]) were synthesized. The structures of the resulting ILs were confirmed by ^{1}H NMR spectroscopy (Bruker Advance 500, Bruker BioSpin) and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics) measurements. The resulted ^{1}H-NMR results and IR spectra are shown below.

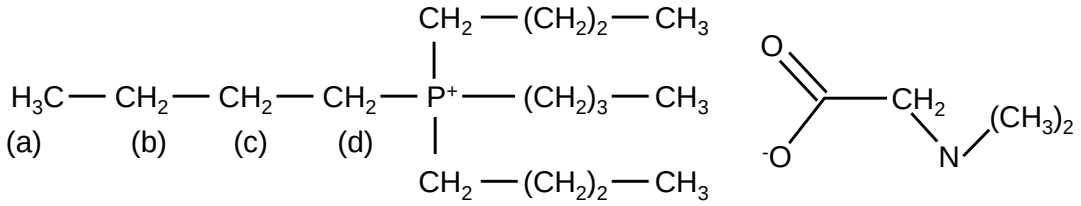
[P_{4444}][Gly]
^{1}H-NMR (DMSO, σ/ppm relative to TMS)
σ = 0.92 (t, 12H, J = 7.1; a), 1.37-1.50 (m, 16H; b,c), 2.08 (s, 1H; acetonitrile), 2.16-2.22 (m, 8H; d), 2.50-2.51 (m, 1H, DMSO), 2.64 (s, 2H; N-CH_2-CO_2), 3.16 ppm (s, 3H; water)



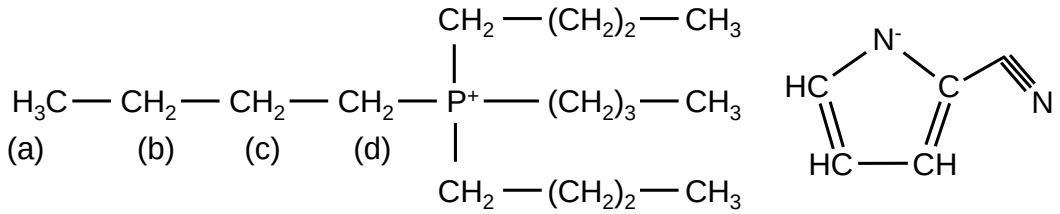
[P_{4444}][mGly]
^{1}H-NMR (DMSO, σ/ppm relative to TMS)
σ = 0.92 (t, 12H, J = 7.3; a), 1.05 (t, 6H, J = 6.0; ethanol), 1.37-1.51 (m, 16H; b,c), 2.19 (s, 3H; N-CH_3), 2.20-2.28 (m, 8H; d), 2.65 (s, 2H; N-CH_2-CO_2), 3.44 ppm (dd, 4H; ethanol)



[P_{4444}][dmGly]
^{1}H-NMR (DMSO, σ/ppm relative to TMS)
σ = 0.92 (t, 12H, J = 7.1; a), 1.37-1.51 (m, 16H; b,c), 2.12 (s, 6H; N-$(CH_3)_2$), 2.17-2.23 (m, 8H; d), 2.50-2.51 (m, 1H, DMSO), 2.52 (s, 2H; N-CH_2-CO_2), 3.17 ppm (s, 2H; water)



[P_{4444}][2-CNpyr]
^{1}H-NMR (DMSO, σ/ppm relative to TMS)
σ = 0.92 (t, 12H, J = 7.1; a), 1.37-1.49 (m, 16H; b,c), 2.13-2.19 (m, 8H; d), 5.82 (dd, 1H, J = 3.15, 1.58; H on the cyanopyrrolide ring), 6.43 (dd, 1H, J = 3.15, 1.26; H on the cyanopyrrolide ring), 6.67 ppm (t, 1H, J = 1.26; H on the cyanopyrrolide ring)



(2) FT-IR data of the ILs synthesized in this study

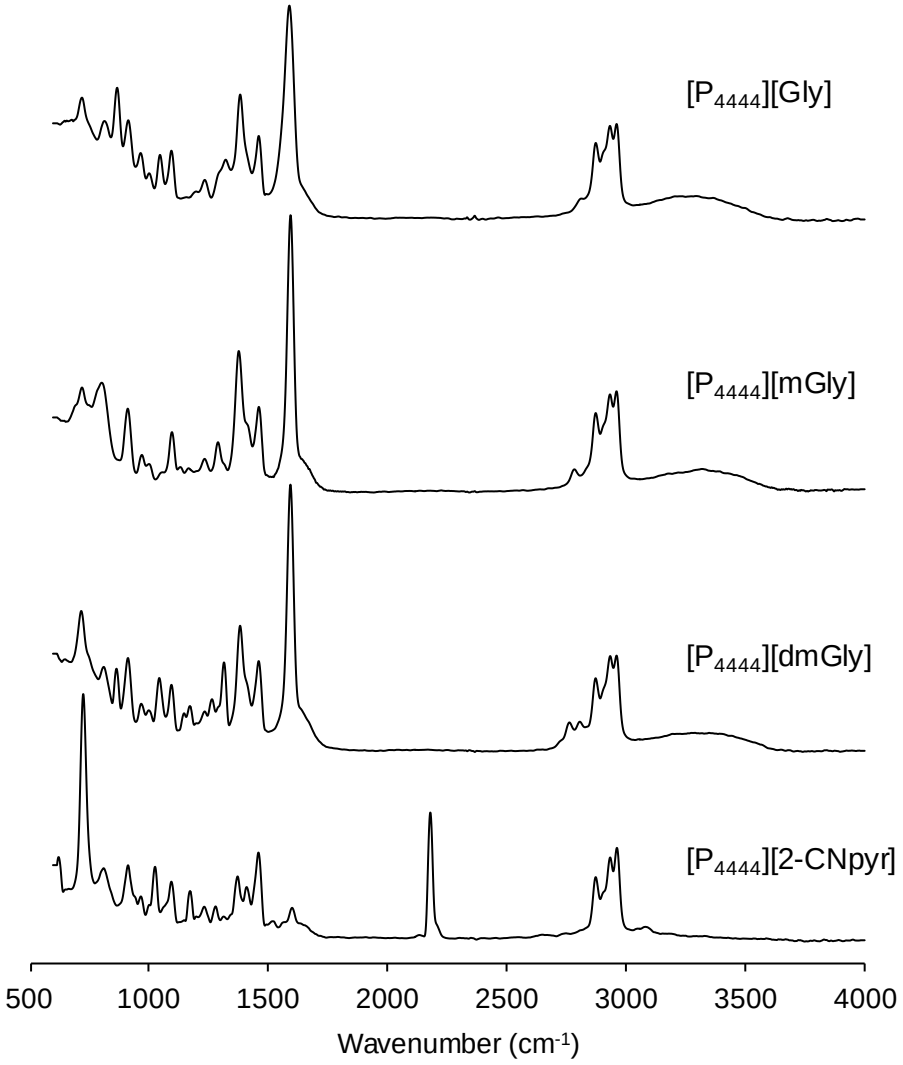


Figure S1. FT-IR spectra of $[P_{4444}]$[Gly], $[P_{4444}]$[mGly], $[P_{4444}]$[dmGly] and $[P_{4444}]$[2-CNpyr].

(3) The effect of CO_2 partial pressure on gas permeation properties of IL-based membranes

Table S1. Experimental conditions of gas permeation test to investigate the CO_2 partial pressure dependency

Conditions	Gases	
Temperature		373 K and 303 K (only [P_{4444}][2-CNpyr]-based membrane)
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO_2	2.5, 5.0, 10, 25, 50, 75 kPa
Pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm^3/min
	CO_2	5, 10, 20, 50, 100, 150 cm^3/min
	N_2	Balance
Sweep	He	40 cm^3/min
Water flow rate	Feed	0 cm^3/min
	Sweep	0 cm^3/min

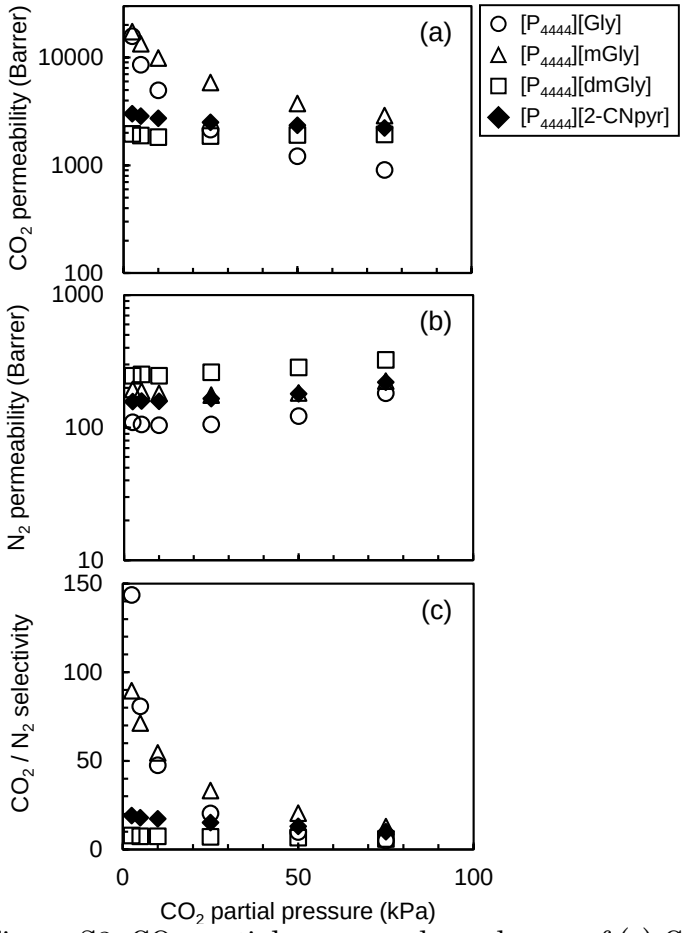


Figure S2. CO_2 partial pressure dependences of (a) CO_2 permeability, (b) N_2 permeability, (c) CO_2/N_2 selectivity for $[P_{4444}]$[Gly]-, $[P_{4444}]$[mGly]-, $[P_{4444}]$[dmGly]-, and $[P_{4444}]$[2-CNpyr]-based membranes at 373 K.

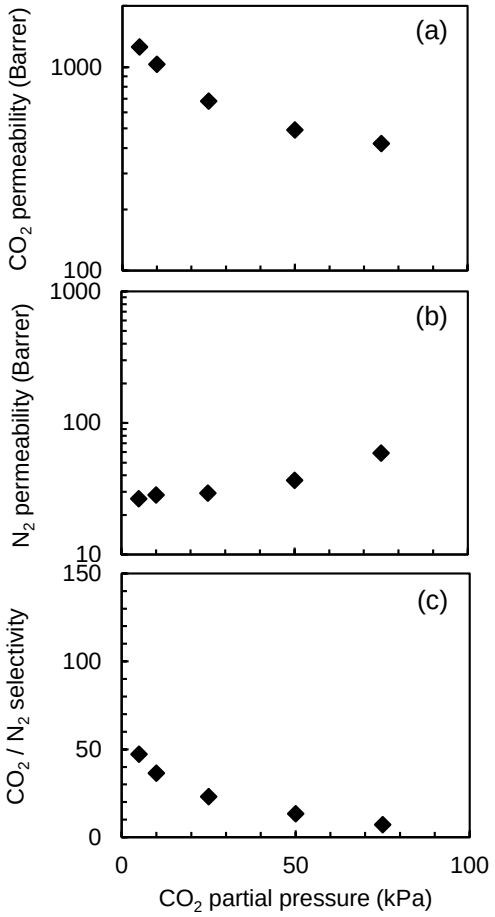


Figure S3. CO_2 partial pressure dependences of (a) CO_2 permeability, (b) N_2 permeability, (c) CO_2/N_2 selectivity for $[P_{4444}]$[2-CNpyr]-based membrane at 303 K.

(4) Comparison of gas separation performance

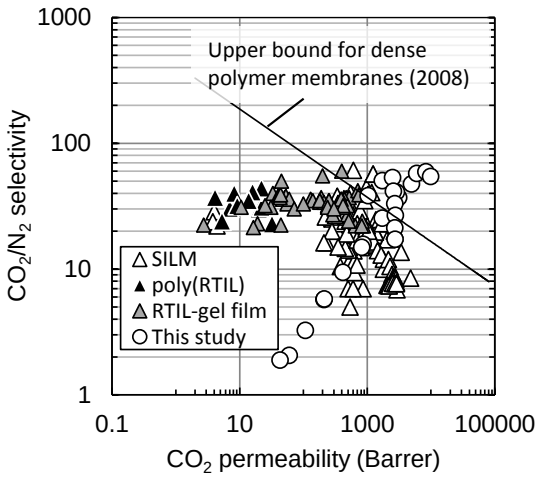


Figure S4. Comparison of gas separation performance for various ionic liquid-based membranes.

(5) The effect of relative humidity on gas permeation properties of IL-based membranes

Relative humidity dependence on gas permeability and selectivity were investigated. The experimental condition for the investigation are shown in Table S2 and the corresponding result are shown in Figure S5. As shown in Figure S5, the CO_2 permeabilities of all membranes increased with increasing relative humidity. Especially, the CO_2 permeabilities of [P_{4444}][dmGly] and [P_{4444}][2-CNpyr] were strongly affected by relative humidity in the gas. The difference in CO_2 permeability would reflect a change in reaction between TSILs and CO_2. When the gas is wet, it was reported that CO_2 and amine carrier react to form bicarbonate.

Table S2 Experimental conditions of gas permeation test to investigate the relative humidity dependency

Conditions	Gases	
Temperature		373 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Pressure difference		0 kPa
Gas flow rate (wet base)		
Feed	Total	200 cm^3/min
	Steam	5.4, 10.9, 20.4, 40.8 cm^3/min
Gas flow rate (dry base)		
Feed	CO_2	4 cm^3/min
	N_2	balance
Sweep	He	40 cm^3/min
Water flow rate	Feed	0.004, 0.008, 0.015, 0.03 cm^3/min
	Sweep	0 cm^3/min
Relative humidity	Feed	2.7, 5.4, 10, 20, 30, 40, 50%

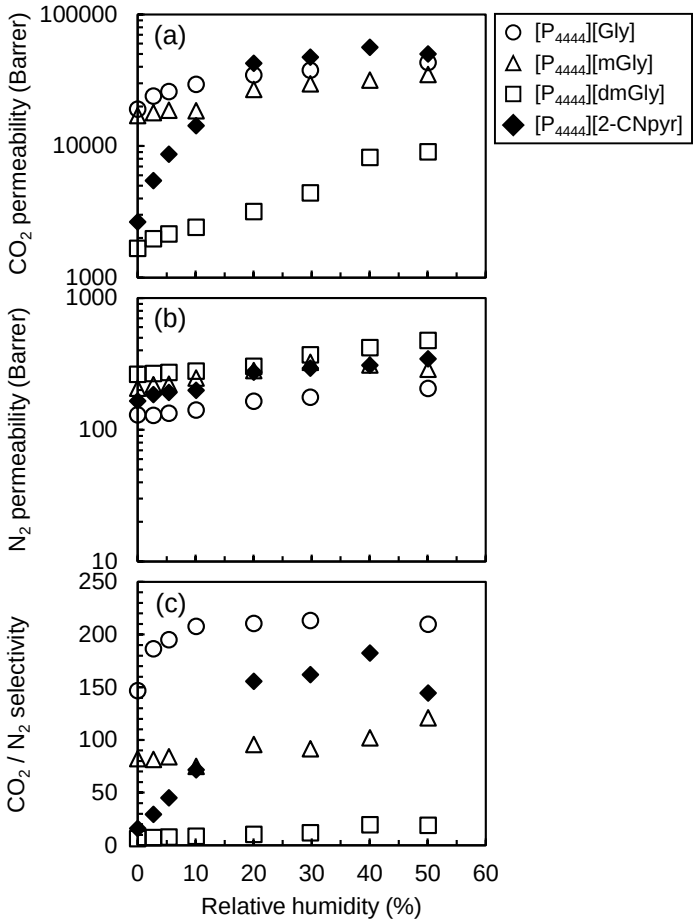


Figure S5. Relative humidity dependences on (a) CO_2 permeability, (b) N_2 permeability and (c) CO_2/N_2 selectivity for $[P_{4444}]$[Gly]-, $[P_{4444}]$[mGly]-, $[P_{4444}]$[dmGly]-, and $[P_{4444}]$[2-CNpyr]-based membranes.