Supplementary Information

Ionic liquid-based materials: a platform to design engineered CO_2 separation membranes

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List of Abbreviations

AA	Amino Acid
AAILs	Amino Acid-based Ionic Liquids
AMP	2-amino-2-methyl-1-propanol
CCS	Carbon Capture and Storage
DEA	Diethanolamine
DMPEG	Copolymer of polyethylene glycol mono and dimethacrylates
DOE	Department of Energy
FTIR	Infrared Spectroscopy
GHGs	Greenhouse Gases
IEA	International Energy Agency
ILs	Ionic Liquids
Im-PEKs	imidazolium functionalized poly(ether ketone)s
IPCC	Intergovernmental Panel on Climate Change
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MMD	Membrane Material Design
MMMs	Mixed Matrix Membranes
MOFs	Metal Organic Frameworks
MSE	Membrane Systems Engineering
NETL	National Energy Technology Laboratory
NMR	Nuclear Magnetic Resonance
PBI	Polybenzimidazole
PEG	Poly(ethylene glycol)
PES	Polyethersulfone
PI	Polyimide
PILs	Poly(ionic liquid)s
PLM	Polarized Light Microscopy
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide)
PS-PIL-PS	Poly(styrene-b-1-[(2-acryloyloxy)ethyl]-3-butylimidazolium bis(trifluoromethylsulfonyl)-imide-b-styrene)
PVC	Poly(vinyl chloride)
PVDF-HFP	Poly(vinylidene fluoride-hexafluoropropyl) copolymer
RH	Relative Humidity

SEM	Scanning Electron Microscopy
SILMs	Supported ionic liquid membranes
SMS	Poly(styrene-b-methyl methacrylate-b-styrene
SOS	Poly(styrene-b-ethylene oxide-b-styrene)
Syngas	Synthesis gas
UV	Ultraviolet
CO_2	Carbon Dioxide
N_2	Nitrogen
H_2	Hydrogen
CH_4	Methane
H_2O	Water
O_2	Oxygen
CO	Carbon Monoxide
SO_x	Sulphur Oxides
H_2S	Hydrogen Sulfide
P	Permeability
D	Diffusivity
S	Solubility
J	Steady-state gas flux
Δp	Trans-membrane pressure drop
p_2	Upstream pressure
p_1	Downstream pressure
ℓ	Membrane thickness
C	Concentration
$\alpha_{i/j}$	Permselectivity
$[R_nmim]^+$	1-Alkyl-3-methylimidazolium
$[R_nmthiaz]^+$	1-Alkyl-3-methylthiazolium
$[R_nmtriaz]^+$	1-Alkyl-3-methyltriazolium
$[R_npy]^+$	1-Alkylpyridinium
$[R_nmpyr]^+$	1-Alkyl-3-methylpyrrolidinium
$[R_nmpip]^+$	1-Alkyl-3-methylpiperidinium
$[Ch]^+$	Cholinium
$R_n[mim]_2^+$	1,*n*-di(3-methylimidazolium)alkyl
$[P_{m.n.o.p}]^+$	Tetraalkylphosphonium
$[N_{m.n.o.p}]^+$	Tetraalkylammonium

$[NTf_2]^-$	Bis(trifluoromethylsulfonyl)amide
$[BETI]^-$	Bis(perfluoroethylsulfonyl)amide
$[PF_6]^-$	Hexafluorophosphate
$[FAP]^-$	Tris(pentafluoroethyl)trifluorophosphate
$[BF_4]^-$	Tetrafluoroborate
$[R_nSO_4]^-$	Alkylsulfate
$[R_nSO_3]^-$	Alkylsulfonate
$[R_nR_nPO_4]^-$	Alkylphosphate
$[Ac]^-$	Acetate
$[Lev]^-$	Levulinate
$[Lac]^-$	Lactate
$[Glyc]^-$	Glycolate
$[Mal]^-$	Malonate
$[Gly]^-$	Glycinate
$[Pro]^-$	Prolinate
$[Ala]^-$	Alaninate
$[Ser]^-$	Serinate
$[mGly]^-$	Methylglycinate
$[SCN]^-$	Thiocyanate
$[N(CN)_2]^-$	Dicyanamide
$[C(CN)_3]^-$	Tricyanomethanide
$[B(CN)_4]^-$	Tetracyanoborate
$[2\text{-}CNpyr]^-$	2-cyanopyrrolide
$[Br]^-$	Bromide
$[Cl]^-$	Chloride
$[CoCl_4]^{2-}$	Tetrachlorocobalt
$[MnCl_4]^{2-}$	Tetrachloromanganese
$[GdCl_6]^{3-}$	Hexachlorogadolinium
$[FeCl_4]^-$	Tetrachloroferrate

Table S1 Gas permeabilities (*P*) and permselectivities ($\alpha_{i/j}$) of SILMs having different cations combined with fluorinated anions.

IL	Membrane support	Measurement conditions	Gas Permeability (Barrer)				Permselectivity ($\alpha_{i/j}$)			Ref.
			P CO_2	***P*** CH_4	***P*** N_2	***P*** H_2	α CO_2/CH_4	α CO_2/N_2	α CO_2/H_2	
Imidazolium										
$[C_4mim][PF_6]$	Hydrophobic PVDF	30 ºC, 0.5 bar single gas	171	–	7.6	27.1	–	23	6.3	[1]
$[C_6mim][PF_6]$			281	–	10.0	36.1	–	28	7.8	
$[C_8mim][PF_6]$			370	–	16.6	68.2	–	22	5.4	
$[C_4mim][BF_4]$	Hydrophobic PVDF	30 ºC, 0.7 bar single gas	390	3.4	9.6	33.7	113	35	11.6	[2]
$[C_{10}mim][BF_4]$			506	7.2	22.3	77.1	69	22	6.6	
$[C_2mim][BF_4]$	PES	30 ºC, 2 bar single gas	968	–	–	–	22	44	–	[3]
$[C_2mim][CF_3SO_3]$			1171	–	–	–	18.5	40.5	–	
$[C_2mim][NTf_2]$			1702	–	–	–	12.2	23	–	
$[C_6mim][NTf_2]$			1136	–	–	–	8.5	15	–	
$[C_4mim][BETI]$			991	–	–	–	9.9	16.7	–	
$[C_2mim][CF_3SO_3]$	Hydrophobic PVDF	30 ºC, 2 bar single gas	486	21.1	14.3	37.2	23.1	34.0	13.1	[4]
$[C_2mim][NTf_2]$	Anodic alumina	23 ºC, 1.15 bar single gas	2640	–	–	–	–	20	–	[5]
$[C_6mim][NTf_2]$			1800	–	–	–	–	12	–	
Thiazolium										
$[C_4mthiaz][NTf_2]$	PES	25 ºC, 0.35 bar single gas	362	–	–	–	–	28	–	[6]
$[B_zmthiaz][NTf_2]$			235	–	–	–	–	21	–	
$[C_3H_7O_2mthiaz][NTf_2]$			248	–	–	–	–	18	–	

$[C_2H_5Omthiaz][NTf_2]$			284	–	–	–	–	25	–	
$[C_2H_5OC_2mthiaz][NTf_2]$			435	–	–	–	–	36	–	
$[C_2H_5OB_zmthiaz][NTf_2]$			96	–	–	–	–	12	–	
Triazolium										
$[i\text{-}C_3mtriaz][NTf_2]$	PES	25 ºC, 0.35 bar single gas	641	–	–	–	–	24	–	
$[C_3mtriaz][NTf_2]$			786	–	–	–	–	28	–	
$[C_4mtriaz][NTf_2]$			483	–	–	–	–	22	–	
$[C_6mtriaz][NTf_2]$			804	–	–	–	–	22	–	
$[C_8mtriaz][NTf_2]$			859	–	–	–	–	17	–	
Pyridinium				–	–	–	–		–	
$[B_zpy][NTf_2]$	Hydrophobic PTFE	25 ºC, 0.35 bar single gas	518	–	18.4	–	–	27.9	–	[7]
$[B_z2mpy][NTf_2]$			358	–	10.8	–	–	33.1	–	
$[B_z3mpy][NTf_2]$			446	–	20.3	–	–	22.0	–	
$[B_z4mpy][NTf_2]$			496	–	21.9	–	–	22.6	–	
$[C_2mpy][(PFOc)SO_3]$	PES	20 ºC, 0.75 bar single gas	897	135	73	–	6.6	12.3	–	[8]
Pyrrolidinium										
$[C_{12}mpyr][NTf_2]$	Hydrophobic PVDF	20 ºC, 1 bar single gas	340	24.2	12.0	–	14.0	28.4	–	[9]
$[B_zmpyr][NTf_2]$	Hydrophobic PTFE	25 ºC, 0.35 bar single gas	280	–	11.0	–	–	25.5	–	[7]
Phosphonium										

$[P_{(14)666}][NTf_2]$	Glass fiber	30 ºC, 0.055 bar single gas	689	169	64	–	4.1	11	–	[10]
Ammonium										
$[N_{(4)111}][NTf_2]$	Glass fiber	30 ºC 0.11 bar single gas	831	63	41	–	13	21	–	[11]
$[N_{(6)111}][NTf_2]$			943	102	46.2	–	9.2	20	–	
$[N_{(10)111}][NTf_2]$			800	105	53.9	–	7.6	11	–	
$[N_{(4)113}][NTf_2]$			724	69	–	–	11	–	–	
$[N_{(6)113}][NTf_2]$			619	74	44	–	8.4	14	–	
$[N_{(10)113}][NTf_2]$			633	114	68	–	5.5	9.4	–	
$[N_{(1)444}][NTf_2]$			524	69	35	–	7.6	15	–	
$[N_{(1)888}][NTf_2]$			619	139	55	–	4.5	11	–	
$[N_{(6)222}][NTf_2]$			630	64	32	–	9.8	20	–	
$[N_{4444}][(PFOc)SO_3]$	PES	20 ºC, 0.75 bar single gas	649	96	56	–	6.7	11.6	–	[8]
Ring-opened										
$[(N_{11})_2CH][NTf_2]$	Anodic alumina	25 ºC, 0.35 bar single gas	1882	–	66	–	–	28	–	[12]
$[(N_{111})_2N][NTf_2]$			1777	–	61	–	–	29	–	

Table S2 Gas permeabilities (*P*) and permselectivities ($\alpha_{i/j}$) of SILMs having functionalized groups attached to the imidazolium cation.

IL	Membrane support	Measurement conditions	Gas Permeability (Barrer)				Permselectivity ($\alpha_{i/j}$)			Ref.
			P CO_2	***P*** CH_4	***P*** N_2	***P*** H_2	α CO_2/CH_4	α CO_2/N_2	α CO_2/H_2	
Aminoalkyl groups										
$[H_2NC_3mim][NTf_2]$	Cross-linked Nylon 66	37 – 95 ºC, 1 bar Mixed gas	100–1000	–	–	–	–	–	0.4–1.4	[13]
$[H_2NC_3mim][NTf_2]$	Hydrophilic PTFE	25 ºC, 0.1 bar Mixed gas	~500	~11	–	–	~45	–	–	[14]
$[H_2NC_3mim][CF_3SO_3]$			~900	~26	–	–	~35	–	–	
Fluoroalkyl groups										
$[C_4F_5mim][NTf_2]$	PES	23 ºC 1 bar Single gas	320	17	12	–	19	27	–	[15]
$[C_6F_9mim][NTf_2]$			280	17	14	–	17	21	–	
$[C_8F_{13}mim][NTf_2]$			210	16	13	–	13	16	–	
Etoxyalkyl groups										
$[C_3H_7Omim][PF_6]$	Hydrophobic PVDF	25 ºC 1.2 bar Single gas	133	–	4	15	–	36	9	[16]
$[C_4H_9Omim][PF_6]$			93	–	5	18	–	20	5	
$[C_6H_{13}O_2mim][PF_6]$			126	–	3	17	–	37	7	
$[C_8H_{17}O_3mim][PF_6]$			109	–	3	16	–	34	7	
Geminal										
$C_3[mim]_2[NTf_2]_2$	alumina	27 ºC, 0.3 bar single gas	190	7	–	–	27	–	–	[17]
$C_6[mim]_2[NTf_2]_2$			230	14	–	–	16	–	–	

Table S3 Gas permeabilities (*P*) and permselectivities ($\alpha_{i/j}$) of SILMs containing different anions.

IL	Membrane support	Measurement conditions	Gas Permeability (Barrer)				Permselectivity ($\alpha_{i/j}$)			Ref.
			P CO_2	*P* CH_4	*P* N_2	*P* H_2	α CO_2/CH_4	α CO_2/N_2	α CO_2/H_2	
Halogen										
$[P_{(14)666}][Br]$	Hydrophobic PVDF	30 ºC, 2 bar single gas	637	76.5	15.3	92.6	8.32	41.5	6.87	4
Phosphates										
$[C_1mim][C_1C_1PO_4]$	Hydrophobic PVDF	30 ºC, 2 bar single gas	127	15.6	11.6	19.9	8.1	10.9	6.4	4
$[P_{2444}][C_2C_2PO_4]$	Glass fiber	30 ºC, 0.055 bar single gas	453	90	31	–	5.0	15	–	10
Sulfonate										
$[P_{(14)444}][DBS]$	Glass fiber	30 ºC, 55 mbar single gas	232	69	14	–	3.4	16	–	10
Sulfates										
$[C_2mim][C_1SO_4]$	Hydrophilic PTFE	20 ºC, 1 bar Single gas	111	3.49	1.59	–	31.7	69.4	–	18
$[C_2mim][C_2SO_4]$			157	7.38	3.06	–	21.2	51.3	–	
Carboxylates										
$[P_{(14)666}][Dec]$			487	65.1	11.3	86.6	7.5	43.1	5.6	4
$[C_2mim][Ac]$	Hydrophobic PVDF	25 ºC, 0.45 bar single gas	879	–	26.1	–	–	33.7	–	19
$[C_4mim][Ac]$			852	–	24.6	–	–	34.6	–	
$[C_2mim][Ac]$	Hydrophilic PTFE	20 ºC, 1 bar Single gas	118	7.26	3.25	–	16.3	36.4	–	20
$[C_2mim][Lac]$			55	3.13	1.27	–	17.6	43.4	–	

[Ch][Mal]	Hydrophilic PTFE	20 ºC, 1 bar Single gas	2	0.09	0.05	–	24.1	39.1	–	21
[Ch][lev]			18	0.84	0.43	–	21.0	41.3	–	
[Ch][Gly]			6	0.16	0.11	–	33.9	50.1	–	
[Ch][Lac]			7	0.33	0.16	–	21.7	46.2	–	
$[N_{(4)222}]$[malonate]	PES	40 ºC, 0.1 bar Saturated gas	2147	–	–	–	198	178	–	22
$[N_{(4)222}]$[maleate]			2840	–	–	–	221	265	–	
Amino Acids										
$[P_{4444}]$[Gly]	Hydrophilic PTFE	100 ºC, 0.1 bar Mixed gas RH = 0 %	~5000	–	~100	–	–	~50	–	23
$[P_{4444}]$[Ala]			~7000	–	~120	–	–	~60	–	
$[P_{4444}]$[Ser]			~2000	–	~60	–	–	~35	–	
$[P_{4444}]$[Pro]			~10500	–	~150	–	–	~70	–	
$[P_{4444}]$[Pro]		RH = 20%	~40000	–	~200	–	–	~200	–	
Magnetic										
$[P_{(14)666}]_2^+[CoCl_4]^{2-}$	Hydrophobic PVDF	25 ºC, 0.45 bar single gas	147	–	6.3	–	–	23.2	–	24
$[P_{(14)666}]^+[FeCl_4]^-$			259	–	10.7	–	–	24.2	–	
$[P_{(14)666}]_2^+[MnCl_4]^{2-}$			203	–	4.9	–	–	41.2	–	
$[P_{(14)666}]_3^+[GdCl_6]^{3-}$			176	–	5.7	–	–	30.8	–	
Cyano										
$[C_2mim][N(CN)_2]$	Hydrophilic PVDF	30 ºC, 2 bar single gas	1237	–	–	–	23	57	–	3
$[P_{(14)666}][N(CN)_2]$	Glass fiber	30 ºC, 0.055 bar single gas	514	108	36	–	4.8	14	–	10
$[(N_{111})_2N][C(CN)_3]$	Anodic alumina	25 ºC, 0.35 bar	1760	–	39	–	–	45	–	12

		single gas								
$[C_2mim][B(CN)_4]$	PES	25 ºC, 0.35 bar	2040	–	38	–	–	53	–	[25]
$[C_4mim][B(CN)_4]$		single gas	1755	–	44	–	–	40	–	
$[C_4mpyr][B(CN)_4]$			1633	–	44	–	–	38	–	
$[C_4mpip][B(CN)_4]$			961	–	26	–	–	37	–	
$[C_2mim][SCN]$	Hydrophilic PTFE	20 ºC, 1 bar Single gas	263	12.1	4.65	–	21.8	56.6	–	[18]
$[C_2mim][N(CN)_2]$			476	20.7	7.03	–	23.0	67.8	–	
$[C_2mim][C(CN)_3]$			667	34.4	11.7	–	19.4	57.0	–	
$[C_2mim][B(CN)_4]$			742	39.0	15.1	–	19.1	49.0	–	
Anion Mixtures										
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	Hydrophilic PTFE	20 ºC, 1 bar Single gas	336	18.9	10.0	–	17.7	33.4	–	[20]
$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$			265	14.6	7.20	–	18.2	36.8	–	
$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$			589	30.9	14.1	–	19.1	41.8	–	
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$			516	25.7	14.1	–	20.1	36.6	–	
$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$			142	6.88	2.29	–	20.6	61.7	–	[18]
$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$			207	8.57	3.56	–	24.1	58.2	–	
$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$			346	18.5	7.38	–	18.7	46.9	–	
$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$			373	18.3	7.20	–	20.3	51.8	–	
$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$			324	14.7	5.29	–	22.1	61.2	–	
$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$			332	16.2	5.78	–	20.5	57.4	–	
$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$			445	23.0	8.71	–	19.4	51.1	–	

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