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Electronic Supplementary Information

Highly efficient and reversible SO_2 capture by halogenated carboxylate ionic liquids

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NMR and IR data of the typical carboxylate ILs

$[P_{66614}][C_5H_{11}COO]$**:** ^{1}H NMR ($CDCl_3$): 0.83 (m, 15H, 5×$CH_3$), 1.20-1.59 (m, 54H, 27×CH_2), 2.11 (t, 2H, −CH_2COO), 2.37 (m, 8H, 4×PCH_2) ppm; ^{13}C NMR ($CDCl_3$): 14.0, 14.1, 14.2, 18.7, 19.2, 21.7, 21.8, 22.0, 22.4, 22.5, 22.7, 22.8, 27.2, 27.7, 28.4, 29.1, 29.2, 29.4, 29.6, 29.7, 30.5, 30.7, 30.8, 30.9, 31.0, 31.2, 31.3, 31.4, 32.0, 32.5, 39.6, 179.3 (C=O) ppm; IR: 2955, 2923, 2854, 1578, 1465, 1417, 1376, 1301, 1262, 1213, 1162, 1110, 984, 914, 891, 865, 809, 721cm^{-1}.

$[P_{66614}][2\text{-}BrC_5H_{10}COO]$**:** ^{1}H NMR (DMSO-d6): 0.85 (m, 15H, 5×CH_3), 1.23-1.47 (m, 54H, 27×CH_2), 2.25 (m, 8H, 4×PCH_2), 4.55 (t, 1H, −CHBrCOO) ppm; ^{13}C NMR (DMSO-d6): 13.7, 13.8, 14.0, 17.2, 17.3, 17.7, 17.8, 20.5, 20.6, 21.2, 21.8, 21.9, 22.1, 22.3, 27.7, 28.1, 28.7, 29.0, 29.7, 29.8, 29.9, 30.1, 30.2, 30.4, 30.8, 31.3, 34.7, 50.3, 176.0 (C=O) ppm; IR: 2956, 2924, 2855, 1742, 1616, 1465, 1409, 1378, 1301, 1264, 1212, 1188, 1132, 1111, 1093, 1048, 989, 891, 862, 809, 720 cm^{-1}

$[P_{66614}][6\text{-}ClC_5H_{10}COO]$**:** ^{1}H NMR (DMSO-d6): 0.85 (m, 12H, 4×CH_3), 1.23-1.51 (m, 54H, 27×CH_2), 2.25 (m, 10H, 4×PCH_2, −CH_2COO), 3.95 (t, 2H, −CH_2Cl) ppm; ^{13}C NMR (DMSO-d6): 13.7, 13.8, 14.0, 17.2, 17.3, 17.7, 18.0, 20.5, 20.6, 21.2, 21.8, 21.9, 22.1, 24.0, 26.4, 28.1, 28.4, 28.7, 28.9, 29.0, 29.1, 29.7, 29.9, 30.1, 30.4, 30.8, 31.3, 33.3, 33.6, 43.4, 172.6 (C=O) ppm; IR: 2955, 2924, 2855, 1735, 1580, 1465, 1416, 1378, 1300, 1250, 1214, 1164, 1111, 1043, 988, 891, 862, 811, 721 cm^{-1}

$[P_{66614}][6\text{-}BrC_5H_{10}COO]$**:** ^{1}H NMR (DMSO-d6): 0.85 (m, 12H, 4×CH_3), 1.24-1.49 (m, 54H, 27×CH_2), 2.26 (m, 10H, 4×PCH_2, −CH_2COO), 3.32 (t, 2H, −CH_2Br) ppm; ^{13}C NMR (DMSO-d6): 13.7, 13.8, 14.0, 17.2, 17.3, 17.7, 17.8, 20.5, 20.6, 21.2, 21.8, 21.9, 22.1, 24.0, 27.8, 28.1, 28.7, 28.9, 29.0, 29.1, 29.7, 29.8, 29.9, 30.1, 30.4, 30.8, 31.3, 32.2, 33.3, 33.5, 174.5(C=O) ppm; IR: 2955, 2924, 2855, 1734, 1579, 1465, 1415, 1378, 1300, 1250, 1214, 1166, 1111, 1044, 988, 891, 862, 811, 720 cm^{-1}.

Table S1. Physical properties of carboxylate ILs for SO_2 capture. [a]

Ionic liquid	d / g cm^{-3}	η / cP	T_m / °C	T_{dec} / °C
$[P_{66614}][C_5H_{11}COO]$	0.9072	108.0	-68	240
$[P_{66614}][6\text{-}BrC_5H_{10}COO]$	0.9664	293.5	-63	279
$[P_{66614}][2\text{-}BrC_5H_{10}COO]$	0.9642	493.0	-64	305
$[P_{66614}][6\text{-}ClC_5H_{10}COO]$	0.9228	187.6	-62	277

[a] d is the density and η is the viscosity measured at 25°C. T_m is the melting point measured from DSC. T_{dec} is the decomposition temperature corresponding to a 10% mass loss measured using TGA.

Table S2. The effect of water constituent on SO_2 capture by acylamino-based ILs.[a]

Ionic liquid	Water loading [b] (mole/mole IL)	SO_2 dry (mole/mole IL)	SO_2 wet [b,c] (mole/mole IL)
$[P_{66614}][C_5H_{11}COO]$	1.76	3.82	3.28
$[P_{66614}][6\text{-}BrC_5H_{10}COO]$	2.20	4.34	4.20
$[P_{66614}][2\text{-}BrC_5H_{10}COO]$	1.64	3.97	3.83
$[P_{66614}][6\text{-}ClC_5H_{10}COO]$	1.99	4.28	4.11

[a] Performed at 20 °C and 1 bar for 30 min. [b] Relative humidity is 100%. [c] Does not include mass of loaded water.

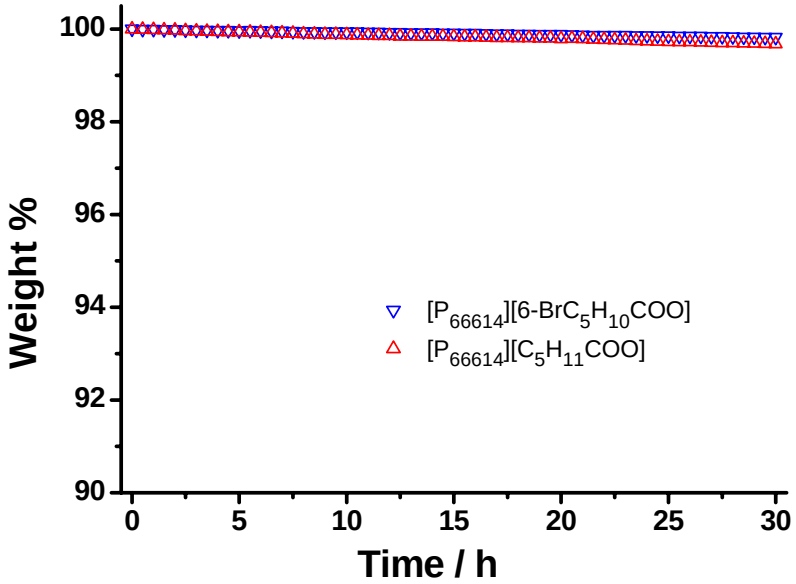

Fig. S1 The thermal stability of $[P_{66614}][6\text{-}BrC_5H_{10}COO]$ and $[P_{66614}][C_5H_{11}COO]$ as a function of time under typical desorption condition (120 °C, 1.0 bar, 60 ml min^{-1} N_2) for 30 h.[1]

Table S3. The comparison of SO_2 absorption by anion-functionalized ILs.

ILs [a]	Temperature/ °C		Available SO_2 absorption at 1 atm[c]	Reference
	Absorption	Desorption[b]		
$[P_{66614}][6\text{-}BrC_5H_{10}COO]$	20	120	4.34	This Work
$[P_{66614}]$[4-Br-PhCOO]	20	120	4.12	Wang[2]
$[P_{66614}][BrCH_2COO]$	20	120	3.89	Wang[2]
$[P_{66614}]$[Tetz]	20	80	3.72	Wang[3]
[Emim][SCN]	20	80	2.99	Wang[4]
[K(TX-7)][SCN]	20	80	3.96	Wang[5]
$[Bmim][BF_4]$	20	20 [e]	1.50	Riisager[6]
$[Bmim][Tf_2N]$	20	20 [e]	1.33	Riisager[6]
$[TMGBu_2][Tf_2N]$	20	20 [e]	1.52	Riisager[6]
[TMG][L]	40 [d]	100	1.34	Han[7], Kim[8]
[TMG][PhO]	20	100 [e]	1.78	Zhang[9]
[TMG][TE]	20	100 [e]	2.93	Zhang[9]
$[E_1mim][MeSO_3]$	30	100	2.30	Kim[8]
$[Bmim][MeSO_4]$	50	130 [f]	0.98	Jung[10]
$[Bmim][CH_3COO]$	25	130 [f]	1.31	Shiflett[11], Jung[10]

[a] $[P_{66614}][6\text{-}BrC_5H_{10}COO]$, trihexyl(tetradecyl)phosphonium 6-bromo-*n*-hexanoate;
$[P_{66614}][BrCH_2COO]$, trihexyl(tetradecyl)phosphonium bromoacetate;
$[P_{66614}]$[4-Br-PhCOO], trihexyl(tetradecyl)phosphonium 4-bromobenzoate;
$[P_{66614}]$[Tetz], trihexyl(tetradecyl)phosphonium tetrazolate;
[Emim][SCN], 1-ethyl-3-methylimidazolium thiocyanate;
[K(TX-7)][SCN], 4-nonylphenyl-polyethylene glycol potassium thiocyanate;
$[Bmim][BF_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate;
$[Bmim][Tf_2N]$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide;
$[TMGB_2][Tf_2N]$, tetramethydibutylguandinium bis(trifluoromethylsulfonyl)imide;
[TMG][L], 1,1,3,3-tetramethyguandinium lactate;
[TMG][PhO], 1,1,3,3-tetramethyguandinium phenolate;
[TMG][TE], 1,1,3,3-tetramethyguandinium trifluoroethoxylate;
$[E_1mim][MeSO_3]$, 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate;
$[Bmim][MeSO_4]$, 1-butyl-3-methylimidazolium methylsulfate;
$[Bmim][CH_3COO]$, 1-butyl-3-methylimidazolium acetate.

Table S4. The halogen group in anion-functionalized ILs on SO_2 absorption enthalpies of anion-SO_2 complexes.

Anion	The absorption enthalpy (kJ mol^{-1})		
	ΔH_1 (CO···S)	ΔH_2 (CO···S)	ΔH_3 (X···S)
[6-$BrC_5H_{10}COO$]	–102.0	–60.17	–13.8
[6-$ClC_5H_{10}COO$]	–101.7	–59.3	–9.4
[2-$BrC_5H_{10}COO$]	–88.3	–56.2	–28.3
[$C_5H_{11}COO$]	–102.6	–60.18	-

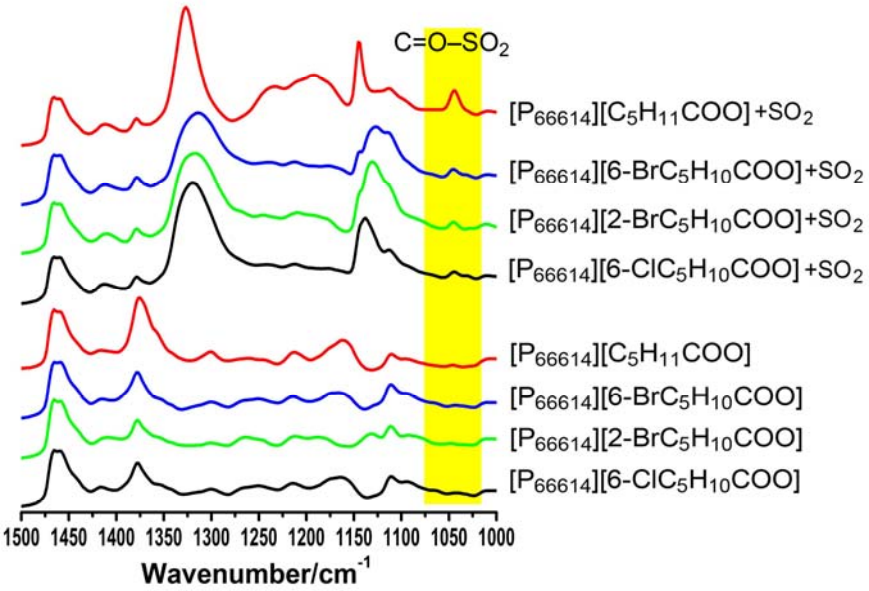

Fig. S2 The FT-IR spectra of [P_{66614}][$C_5H_{11}COO$], [P_{66614}][6-$BrC_5H_{10}COO$], [P_{66614}][2-$BrC_5H_{10}COO$], and [P_{66614}][6-$ClC_5H_{10}COO$] after the absorption of SO_2 at 20 °C and 1 bar to show the CO···SO_2 interactions clearly.

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