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Experimental Section

Synthesis of [BzMim][Tf_2N].

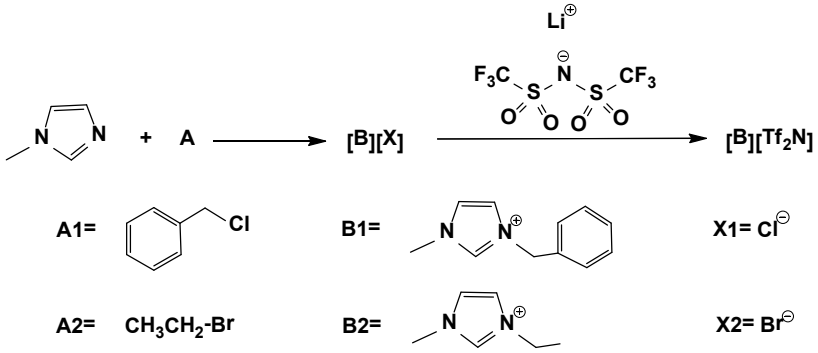

Figure A1. Synthetic route of [BzMim][Tf_2N] and [EMim].

[BzMim][Tf_2N] was synthesized according to Figure A1. In a 250 ml three-necked flask, 1-methylimidzole (16.42 g, 0.2 mol) was slowly added dropwise to benzyl chloride (25.32 g, 0.2 mol) at room temperature with vigorous stirring, and the reaction mixture became cloudy and viscous. A clear yellow gel formed after the addition was completed. Then 50 ml deionized water was added to dissolve. $LiTf_2N$ (57.42 g, 0.2 mol) predissolved in 50 ml deionized water was slowly added dropwise to this aqueous solution with stirring for 2 h at room temperature. After the mixture had standed, the top phase was decanted, and the lower phase was separated, which was dissolved in 50 ml CH_2Cl_2 and washed with deionized water until no Cl^- could be detected. The product was concentrated under reduced pressure at 60 °C to remove CH_2Cl_2 and dried under high vacuum at 90 °C for 24 h to give [BzMim][Tf_2N] (42.76 g, 47.16 %) as a colorless liquid. The sample was kept in glass vial, closed with screw cap to ensure a secure seal and prevent humidity.

Synthesis of [EMim][Br].

[EMim][Br] was prepared by the same procedure reported by the literature.[1] 1-Methylimidazole (16.42 g, 0.20 mol) and bromoethane (26.15 g, 0.24 mol) were used, and [EMim][Br] (36.3 g, 95 %) as a white solid was obtained after the reaction. The sample was kept in glass vial, closed with screw cap to ensure a secure seal and prevent humidity.

***Synthesis of* [EMim][Tf_2N].**

[EMim][Tf_2N] was synthesized from [EMim][Br] and $LiTf_2N$ by the same procedure used as for [BzMim][Tf_2N]. [EMim][Br] (38.21 g, 0.2 mol) was dissolved by 50 ml deionized. $LiTf_2N$ (57.42 g, 0.2 mol) predissolved in 50 ml deionized water was slowly added dropwise to this aqueous solution with stirring for 2 h at 70 °C. After the mixture had standed, the top phase was decanted, and the lower phase was separated, which was dissolved in 50 ml CH_2Cl_2 and washed with deionized water until no Br^- could be detected. The product was concentrated under reduced pressure at 60 °C to remove CH_2Cl_2 and dried under high vacuum at 90 °C for 24 h to give [EMim][Tf_2N] (55.18 g, 72.3%) as a colorless liquid. The sample was kept in glass vial, closed with screw cap to ensure a secure seal and prevent humidity.

The structures of these ILs were confirmed by NMR and IR spectroscopy; no impurities were found by NMR. The water content of these ILs was determined with a Karl Fisher titration (Mettler Toledo DL32, Switzerland) and found to be less than 0.1 wt%. The residual bromide content of these ILs was determined by a semi-quantitative Nessler cylinder method, which showed that bromide content was lower than 0.15 wt%.

NMR and IR data of ILs

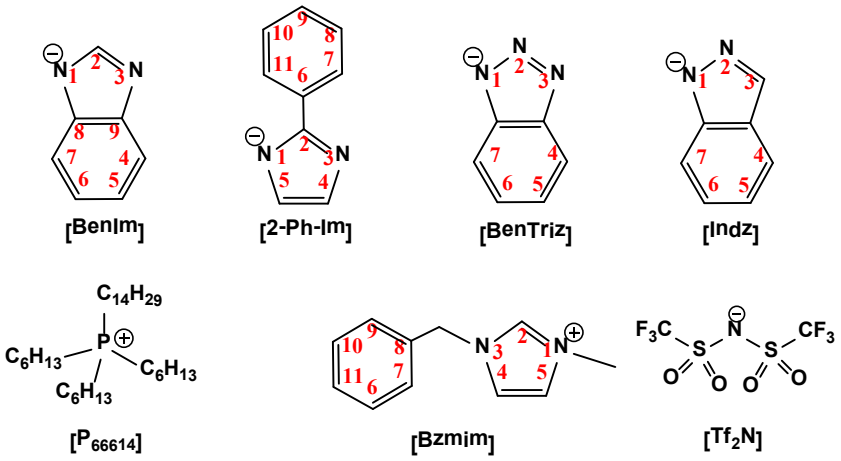

Figure A2. Numbering scheme for positions in the typical ILs.

[P_{66614}][BenIm]: ^{1}H NMR (DMSO-d6): 0.87 (m, 12H, CH_3), 1.20-1.50 (m, 48H, CH_2),

2.12 (m, 8H, PCH_2), 6.70 (m, 2H, C5 and C6), 7.31 (m, 2H, C4 and C7), 7.63 (s, 1H, C2) ppm; ^{13}C NMR (d6-DMSO): 14.2, 14.3, 17.6, 18.1, 21.0, 22.3, 22.6, 28.6, 29.1, 29.2, 29.5, 30.1, 30.2, 30.4, 30.5, 30.9, 31.8, 116.1 (C4 and C7), 116.4 (C5 and C6), 146.7 (C8 and C9), 152.5 (C2) ppm; IR: 3058, 3037, 2955, 2925, 2855, 1594, 1579, 1465, 1416, 1378, 1362, 1303, 1266, 1218, 1175, 1135, 1107, 1000, 914, 882, 771, 739, 720, 695, 683, 673, 660, 645 cm^{-1}. MS: 483.7 for [P_{66614}], 116.9 for [BenIm].

After the absorption of SO_2: ^1H NMR (DMSO-d6): 0.85 (m, 12H, CH_3), 1.20-1.50 (m, 48H, CH_2), 2.18 (m, 8H, PCH_2), 7.21 (m, 2H, C5 and C6), 7.63 (m, 2H, C4 and C7), 8.36 (s, 1H, C2) ppm; ^{13}C NMR (d6-DMSO): 14.3, 14.4, 18.0, 18.4, 21.2, 22.4, 22.7, 28.8, 29.3, 29.6, 30.3, 30.4, 30.2, 30.5, 30.7, 31.0, 31.9, 115.7 (C4 and C7), 122.7 (C5 and C6), 137.6 (C8 and C9), 142.1 (C2) ppm; IR: 2956, 2927, 2856, 1619, 1455, 1412, 1379, 1324, 1269, 1192, 1143, 1040, 1006, 947, 870, 775, 749, 720, 695, 684, 667, 657, 643 cm^{-1}.

[P_{66614}][2-Ph-Im]: ^1H NMR (DMSO-d6): 0.87 (m, 12H, CH_3), 1.20-1.50 (m, 48H, CH_2), 2.12 (m, 8H, PCH_2), 6.74 (s, 2H, C4 and C5), 6.91 (t, 1H, C9), 7.14 (t, 1H, C8 and C10), 7.92 ppm (d, 1H, C7 and C 11); ^{13}C NMR (d6-DMSO): 14.2, 14.3, 17.6, 18.1, 21.0, 22.3, 22.6, 28.6, 29.1, 29.2, 29.5, 30.1, 30.2, 30.3, 30.5, 30.9, 31.8, 123.4 (C6), 124.2 (C4 and C5), 127.6 (C8 and C10), 127.7 (C7 and C11), 139.6 (C9), 152.6 (C2) ppm; IR: 2955, 2925, 2855, 1737, 1663, 1638, 1599, 1577, 1504, 1486, 1457, 1401, 1378, 1269, 1215, 1163, 1132, 1103, 1066, 1054, 1027, 996, 929, 912, 861, 808, 772, 720, 698, 687, 674, 666, 657, 641 cm^{-1}.

After the absorption of SO_2: ^1H NMR (DMSO-d6): 0.85 (m, 12H, CH_3), 1.20-1.60 (m, 48H, CH_2), 2.19 (m, 8H, PCH_2), 7.50-7.80 (m, 5H, C4,C5, C8~10), 8.03 ppm (d, 1H, C7 and C11); ^{13}C NMR (d6-DMSO): 14.3, 14.4, 17.9, 18.3, 21.1, 22.3, 22.6, 28.7, 29.2, 29.5, 29.6, 30.2, 30.3, 30.5, 30.6, 30.9, 31.8, 121.7 (C4 and C5), 125.8 (C6), 126.6 (C8 and C10), 129.8 (C7 and C11), 131.3 (C9), 144.6 (C2) ppm; IR: 2956, 2927, 2856, 1752, 1664, 1630, 1600, 1574, 1519, 1496, 1467, 1427, 1379, 1325, 1143, 1106, 1073, 1041, 1006, 951, 904, 811, 779, 755, 707, 690, 677, 667, 659, 637 cm^{-1}.

[P_{66614}][BenTriz]: ^1H NMR (d6-DMSO): 0.89 (m, 12H, CH_3), 1.20-1.40 (m, 48H, CH_2), 2.12 (m, 8H, PCH_2), 6.83 (m, 2H, C5 and C6), 7.58 (m, 2H, C4 and C7) ppm; ^{13}C NMR (d6-DMSO): 14.1, 14.2, 17.7, 18.1, 21.0, 22.2, 22.5, 28.6, 29.2, 29.4, 29.5, 30.1, 30.2, 30.4, 30.5, 30.8, 31.8, 116.0, 118.9, 145.9 ppm; IR: 2955, 2925, 2855, 1465, 1408,

1381, 1302, 1275, 1215, 1172, 1140, 1121, 1057, 1001, 924, 810, 775, 742, 718, 693, 681, 668, 659, 651, 641 cm^{-1}. MS: 483.7 for [P_{66614}], 117.8 for [BenTriz].

After the absorption of SO_2: ^{1}H NMR (d6-DMSO): 0.85 (m, 12H, CH_3), 1.20-1.50 (m, 48H, CH_2), 2.23 (m, 8H, PCH_2), 7.39 (m, 2H, C5 and C6), 7.95 (m, 2H, C4 and C7) ppm; ^{13}C NMR (d6-DMSO): 14.3, 14.4, 18.0, 18.4, 21.2, 21.3, 22.4, 22.7, 28.8, 29.4, 29.6, 29.7, 30.3, 30.4, 30.6, 30.7, 31.0, 31.9, 115.5, 125.4, 139.4 ppm; IR: 2956, 2928, 2856, 2361, 2342, 1460, 1413, 1378, 1326, 1262, 1209, 1192, 1144, 1045, 1008, 985, 943, 902, 828, 809, 798, 778, 749, 721, 693, 680, 670, 660, 651, 637 cm^{-1}.

[P_{66614}][Indz]: ^{1}H NMR (d6-DMSO): 0.85 (m, 12H, CH_3), 1.20-1.40 (m, 48H, CH_2), 2.10 (m, 8H, PCH_2), 6.73 (t, 1H, C5), 6.91 (t, 1H, C6), 7.48 (d, 1H, C7), 7.54 (d, 1H, C4), 7.89 (s, 1H, C3) ppm; ^{13}C NMR (d6-DMSO): 14.3, 14.4, 17.7, 18.0, 21.0, 21.1, 22.4, 22.6, 28.6, 29.2, 29.2, 29.5, 29.6, 30.2, 30.3, 30.4, 30.5, 30.9, 31.8, 113.9, 116.8, 119.4, 121.2, 124.0, 130.9, 147.2 ppm; IR: 2954, 2924, 2854, 1669, 1465, 1377, 1357, 1277, 1211, 1161, 1110, 1054, 995, 939, 809, 782, 756, 731, 692, 680, 668, 658, 650, 641 cm^{-1}. MS: 483.7 for [P_{66614}], 112.9 for [Indz].

After the absorption of SO_2: ^{1}H NMR (d6-DMSO): 0.87 (m, 12H, CH_3), 1.20-1.40 (m, 48H, CH_2), 2.20 (m, 8H, PCH_2), 7.09 (t, 1H, C5), 7.33 (t, 1H, C6), 7.57 (d, 1H, C7), 7.75 (d, 1H, C4), 8.04 (s, 1H, C3) ppm; ^{13}C NMR (d6-DMSO): 14.3, 14.4, 17.8, 18.2, 21.1, 21.2, 21.8, 22.5, 28.7, 29.3, 29.3, 29.7, 30.3, 30.4, 30.5, 30.6, 31.0, 31.9, 110.7, 120.5, 120.8, 123.3, 126.2, 133.6, 140.5 ppm; IR: 2926, 2856, 2361, 2341, 1734, 1717, 1699, 1684, 1653, 1636, 1623, 1576, 1559, 1540, 1521, 1507, 1458, 1419, 1326, 1204, 1144, 942, 895, 854, 835, 742, 718, 692, 679, 668, 652, 633 cm^{-1}.

[Bzmim][Tf_2N]: ^{1}H NMR (d6-DMSO): 3.88 (s, 3H, CH_3), 5.44 (s, 2H, CH_2), 7.40-7.44 (m, 5H, C7～C9), 7.70 (s, 1H, C4), 7.78 (s, 1H, C5), 9.22 (s, 1H, C2) ppm; ^{13}C NMR (d6-DMSO): 36.3 (CH_3), 52.5 (CH_2), 118.8 (q, J_{C-F} = 322.6 Hz, CF_3), 122.9 (d, J=17.2 Hz, C4), 124.5 (d, J=18.0 Hz, C5), 128.8 (s, C7 and C9), 129.2 (s, C11), 129.5 (s, C6 and C10), 135.3 (s, C8), 137.2 (d, J=9.5 Hz, C2) ppm; IR: 3155, 3115, 1575, 1564, 1499, 1457, 1430, 1350, 1331, 1185, 1135, 1054, 845, 821, 790, 762, 740, 720, 699 cm^{-1}.

After the absorption of SO_2: ^{1}H NMR (d6-DMSO): 3.87 (s, 3H, CH_3), 5.43 (s, 2H, CH_2), 7.39-7.44 (m, 5H, C7～C9), 7.68 (s, 1H, C4), 7.76 (s, 1H, C5), 9.20 (s, 1H, C2)

ppm; ^{13}C NMR (d6-DMSO): 36.4 (CH_3), 52.6 (CH_2), 118.9 (q, J_{C-F} = 322.6 Hz, CF_3), 123.0 (d, J=18.3 Hz, C4), 124.6 (d, J=18.1 Hz, C5), 128.9 (s, C7 and C9), 129.4 (s, C11), 129.6 (s, C6 and C10), 135.3 (s, C8), 137.3 (d, J=9.3 Hz, C2) ppm; IR: 3157, 3119, 2363, 1575, 1563, 1499, 1457, 1430, 1334, 1226, 1188, 1136, 1055, 821, 790, 762, 740, 720, 699 cm^{-1}.

[EMim][Tf$_2$N]: ^{1}H NMR (d6-DMSO): 1.44 (t, 3H, CH_2CH_3), 3.86 (s, 3H, CH_3), 4.20 (q, 2H, CH_2), 7.67 (s, 1H, Im C5), 7.75 (s, 1H, Im C4), 9.11 (s, 1H, Im C2) ppm; ^{13}C NMR (d6-DMSO): 15.4, 36.1, 44.7, 118.8, 121.3, 122.4, 122.5, 124.0, 124.1, 136.8 ppm; IR: 3160, 3123, 2992, 1574, 1456, 1432, 1349, 1332, 1183, 1136, 1089, 1054, 959, 841, 790, 762, 740, 699 cm^{-1}.

After the absorption of SO$_2$: ^{1}H NMR (d6-DMSO): 1.44 (t, 3H, CH_2CH_3), 3.86 (s, 3H, CH_3), 4.20 (q, 2H, CH_2), 7.66 (s, 1H, Im C5), 7.74 (s, 1H, Im C4), 9.09 (s, 1H, Im C2) ppm; ^{13}C NMR (d6-DMSO): 15.5, 36.2, 44.8, 118.9, 121.4, 122.4, 122.6, 124.1, 124.2, 136.8 ppm; IR: 3160, 3123, 2988, 2359, 2342, 1573, 1457, 1431, 1334, 1227, 1187, 1136, 1055, 959, 839, 790, 763, 741, 696 cm^{-1}.

Table S1 The viscosities, densities and melting points of these ionic liquids for SO_2 capture.

Ionic liquids	Viscosity [a] / cP	Density [b] / g cm^{-3}	Melting point/^{o}C
[P_{66614}][BenIm]	713	0.922	-61
[P_{66614}][2-Ph-Im]	1041	0.956	-58
[P_{66614}][BenTriz]	464	0.923	-62
[P_{66614}][Indz]	376	0.906	-61
[P_{66614}][Im]	424	0.915	-60

[a] Measured at 25 ^{o}C; [b] Measured at 30 ^{o}C.

Table S2. The effect of low partial pressure of SO_2, temperature, and water on SO_2 capture by [P_{66614}][BenIm] and [P_{66614}][2-Ph-Im].[a]

Ionic liquids	SO_2 absorption [b]				
	10% SO_2	1% SO_2	2000 ppm SO_2	500 ppm SO_2	100% SO_2 (wet) [c]
[P_{66614}][BenIm]	2.46(1.86)	1.76(1.56)	1.62(1.47)	1.52(1.41)	5.78
[P_{66614}][2-Ph-Im]	2.59(1.92)	1.76(1.52)	1.58(1.37)	1.39(1.30)	5.76

[a.] The absorption was carried out at 20 ^{o}C. [b.] Mole SO_2 per mole IL. [c] Relative humidity is 100%. [d.] Value given in brackets was measured at 40 ^{o}C.

Table S3. The comparison of SO_2 absorption by phenyl-containing azole-based ILs with that by other typical ILs.

Ionic liquids [a]	Temperature/ °C	SO_2 absorption [b]		Reference
		at 1 bar	at 0.1 bar	
$[P_{66614}][BenIm]$	20	5.75 (0.61)	2.46 (0.26)	This work
$[P_{66614}][2\text{-Ph-Im}]$	20	5.74 (0.59)	2.59 (0.26)	This work
$[P_{66614}][Im]$	20	4.80 (0.56)	2.07 (0.24)	Wang[2]
$[P_{444E3}][Tetz]$	20	5.00 (0.76)	1.87 (0.29)	Wang[2]
$[P_{66614}][SCN]$	20	3.24 (0.38)	1.06 (0.13)	Wang[3]
[TMG][L]	40	1.70 (0.53) [c]	0.978 (0.31)	Han[4]
[TMG][PhO]	20	2.58 (0.79)	-	Zhang[5]
[TMG][TE]	20	4.13 (1.23)	-	Zhang[5]
$[TMG][BF_4]$	20	1.27 (0.40)	0.064 (0.02)	Riisager[6]
$[TMGBu_2][Tf_2N]$	20	1.60 (0.20)	0.080 (0.01)	Riisager[6]
$[TMG][Tf_2N]$	20	1.18 (0.19)	0.061 (0.01)	Riisager[6]
$[Bmim][BF_4]$	20	1.50 (0.40)	0.005 (0.001)	Riisager[6]
$[Bmim][MeSO_4]$	50	0.980 (0.25)	-	Jung[7]
[Bmim][OAc]	25	1.91 (0.62)	0.664 (0.21)	Shiflett[8]
$[Bzmim][Tf_2N]$	20	1.51 (0.21)	-	This work
$[Hmim][Tf_2N]$	25	0.916 (0.13)	0.005 (0.0007)	Brennecke[9]
$[E_1mim][MeSO_3]$	30	2.30 (0.62)	-	Kim[10]

[a] $[P_{66614}][BenIm]$, trihexyl(tetradecyl)phosphonium benzimidazolate; $[P_{66614}][2\text{-Ph-Im}]$, trihexyl(tetradecyl)phosphonium 2-phenylimidazolate; $[P_{66614}][Im]$, trihexyl(tetradecyl)phosphonium imidazolate; $[P_{66614}][Tetz]$, trihexyl(tetradecyl)phosphonium tetrazolate; [Emim][SCN], 1-ethyl-3-methylimidazolium thiocyanate; [TMG][L], 1,1,3,3-tetramethylguanidinium lactate; [TMG][PhO], 1,1,3,3-tetramethyguandinium phenolate; [TMG][TE], 1,1,3,3-tetramethyguandinium trifluoroethoxylate; $[TMG][BF_4]$, 1,1,3,3-tetramethyguandinium tetrafluoroborate; $[TMGBu_2][Tf_2N]$, 1,1,3,3-tetramethydibutylguandinium bis(trifluoromethylsulfonyl)imide; $[TMG][Tf_2N]$, 1,1,3,3-tetramethyguandinium bis(trifluoromethylsulfonyl)imide; $[Bmim][BF_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate; $[Bmim][MeSO_4]$, 1-butyl-3-methylimidazolium methylsulfate; [Bmim][OAc], 1-butyl-3-methylimidazolium acetate; $[Bzmim][Tf_2N]$ 1-benzyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[Bmim][Tf_2N]$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[Hmim][Tf_2N]$, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[E_1mim][MeSO_3]$, 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate. [b] mole SO_2/mole IL(g SO_2/g IL). [c] At 1.2 bar.

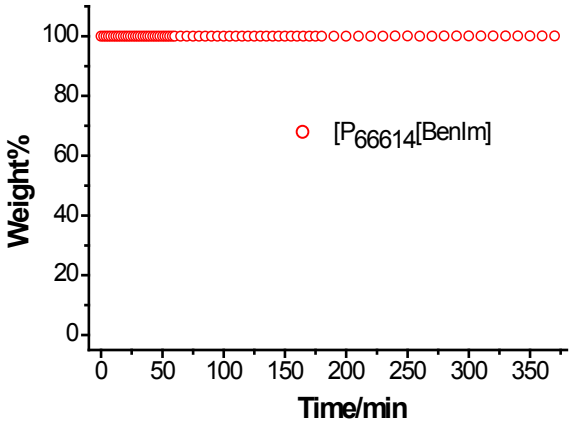

Fig. S1 The stability of $[P_{66614}][BenIm]$ as a function of time at 80 °C under N_2 containing 100 % humidity.

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